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ATMOSPHERIC EMISSIONS FROM CHLOR-ALKALI MANUFACTURE

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The manufacture of chlorine and related products is generally known as the chlor-alkali industry. A description is given of the electrolytic process. Process information includes the discussion of normal process variables that affect the range and quantities of emissions and methods of controlling or reducing emissions. Supplemental material provides detailed emission-sampling and analytical methods. Information is provided on the range of emissions that occur under normal operating conditions and with the use of established methods and devices employed to limit or control emissions from the manufacture of chlorine and caustic. The emissions and operating data results from approximately 15 percent of present establishments, representing a broad range of plant capacities and both diaphragm and mercury cells. Most of these data have been gathered from production records of chlorine and caustic manufacturers.

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PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the National Air Pollution Control Administration (NAPCA) of the United States Department of Health, Education, and Welfare, and the Manufacturing Chemists' Association, Inc., (MCA), entered into an agreement on October 29, 1962, to study emissions from selected chemical manufacturing processes and to publish information that would be helpful to air pollution control and planning agencies and to chemical industry management. Direction of these studies is vested in an MCA-NAPCA Steering Committee, presently constituted as follows:

Representing NAPCA
Stanley T. Cuffe*
Robert L. Harris, Jr.
Dario R. Monti
Raymond Smith

Representing MCA
Willard F. Bixby*
Louis W. Roznoy
Clifton R. Walbridge
Elmer P. Wheeler

Information included in these reports describes the range of emissions under normal operating conditions and the performance of established methods and devices employed to limit and control these emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are both outside the scope of this program.

Reports published to date in this series are:

Atmospheric Emissions from Sulfuric Acid Manufacturing Processes	PHS Publication No. 999-AP-13
Atmospheric Emissions from Nitric Acid Manufacturing Processes	PHS Publication No. 999-AP-27
Atmospheric Emissions from Thermal-Process Phosphoric Acid Manufacture	PHS Publication No. 999-AP-48
Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes	NAPCA Publication No. AP-54
Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture	NAPCA Publication No. AP-57

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*Principal representative.

USE AND LIMITATIONS OF THIS REPORT

This report, one of a series concerning atmospheric emissions from chemical manufacturing processes, has been prepared to provide information on atmospheric emissions from the manufacture of chlorine and caustic. The manufacture of chlorine and related products is generally known as the chlor-akali industry. Although the report centers around the electrolytic production of chlorine and caustic from brine, it also touches upon the use of fused-salt cells for the manufacture of sodium and chlorine, minor chemical processes for the manufacture of chlorine, and the lime-soda method for caustic manufacture. For the purposes of this report, only processes directly involved in the manufacture of chlorine and caustic have been examined.

Background information is included to define the importance of the chlor-alkali industry in the United States. Basic characteristics of the industry are discussed, including growth rate in recent years, manufacturing processes, uses for the products, and the number and location of production sites.

A description is given of the electrolytic process. Process information includes the discussion of normal process variables that affect the range and quantities of emissions and methods of controlling or reducing emissions. Supplemental material provides detailed emission-sampling and analytical methods.

This report provides information on the range of emissions that occur under normal operating conditions and with the use of established methods and devices employed to limit or control emissions from the manufacture of chlorine and caustic. The emissions and operating data in Appendix A are results from approximately 15 percent of present establishments,* representing a broad range of plant capacities and both diaphragm and mercury cells. Most of these data have been gathered from production records of chlorine and caustic manufacturers. Stack tests from four plants conducted during 1967 by the National Air Pollution Control Administration show results consistent with the data received from industry sources

The production of chlorine and caustic, a basic industry in the United States for 50 years, involves well-established manufacturing procedures. Since the industry is growing at a rate double that of the economy, a review of the information in this report will be desirable within the next 5 to 10 years.

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*An establishment is defined as a works having one or more chlor-alkali plants or units, each of which is a complete production entity.

Although this report has been prepared as an industry review primarily for public officials concerned with the control of air pollution, the information may also be helpful to chemical plant management and technical staffs. It may be helpful as well to engineering students, medical personnel, and other professional people interested in emissions from chlor-alkali plants.

ACKNOWLEDGMENTS

Many companies and individuals in the chlorine industry have been helpful in promoting this study; for their contributions, the project sponsors extend their sincere gratitude.

Special thanks are due the following operating companies for their participation in a program of stack sampling specifically for this study:

Hooker Chemical Company
Olin Corporation
Wyandotte Chemical Corporation

The Chlorine Institute, Inc., New York, New York, supplied statistics on the industry.

James C. Knudson and George Crane of the National Air Pollution Control Administration and Raymond S. Briggs of Hooker Chemical Co., subsidiary of Occidental Petroleum Corporation, were the investigators and are the principal authors of this report. The sponsors acknowledge the contribution of the Hooker Chemical Company in providing the services of Mr. Briggs, whose extensive experience in the chlorine industry has proved invaluable.

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ATMOSPHERIC EMISSIONS FROM CHLOR-ALKALI MANUFACTURE

SUMMARY

PRODUCTION OF CHLORINE AND CAUSTIC

During 1969, 9.4 million tons of chlorine and 10 million tons of caustic soda were produced in the United States. The annual rate of production has been increasing at about 8 percent per year. More than 99.5 percent of the chlorine and 94 percent of the caustic soda made in 1969 were produced electrolytically. Less than 0.5 percent of the chlorine was produced chemically. The remaining 6 percent of caustic soda was produced by the lime-soda process. In 1968, diaphragm cells accounted for about 68 percent of chlorine production, mercury cells for about 29 percent, and fused-salt cells for approximately 3 percent.

DESCRIPTION OF PROCESSES

Chlorine and caustic are produced concurrently in electrolytic cells. An electric current decomposes a chloride salt that is usually fed to the cell as a water solution. Chlorine gas is produced at the anode of the cell. In one type of cell, hydrogen is liberated at the cathode and a diaphragm is used to prevent contact of the chlorine produced with the hydrogen or the alkali hydroxide that is formed simultaneously. In another type of cell, liquid mercury is used as the cathode and forms an amalgam with the alkali metal. The amalgam is removed from the cell and is reacted with water in a separate chamber called a denuder to form alkali hydroxide and hydrogen. In another version of the electrolytic process, molten salts are used in place of aqueous solutions.

Both chlorine and hydrogen are produced in the electrolytic cell. Hydrogen gas saturated with water vapor leaves the cell at the top of the cathode compartment, usually with a purity above 99.9 percent (dry basis). In most plants it is cooled to condense moisture, compressed, and used as process hydrogen or fuel. Chlorine gas leaving the cells is saturated with water vapor and cooled to condense some of the water. In diaphragm cell operation, the cooling may be done indirectly or by direct contact with cold water as in a blow-gas absorber. Chlorine gas from mercury cells is usually cooled indirectly with cold water. After water cooling, the gas is further dried by direct contact with strong sulfuric acid. The dry chlorine gas is then compressed for in-plant use or is cooled further by means of refrigeration to liquefy the chlorine. Approximately half of the total chlorine in the United States is produced as liquid chlorine.

The caustic produced in diaphragm-cell plants leaves the cell as a dilute solution along with unreacted brine. The solution is evaporated to increase the concentration to 50 or 73 percent, so that most of the residual salt is precipitated and removed by filtration. In mercury-cell plants, high-purity caustic can be produced in any desired strength and needs no concentration.

EMISSIONS

Emissions to the atmosphere from diaphragm- and mercury-cell chlorine plants include chlorine gas (Cl_2), carbon dioxide (CO_2), and hydrogen (H_2).

Gaseous chlorine is present in the blow gas from liquefaction from vents in tank cars, ton containers, and cylinders during loading and unloading and from storage- and process-transfer tanks. The chlorine content of blow-gas streams normally ranges from 2,000 to 10,000 pounds per 100 tons of chlorine produced for diaphragm cells and from 4,000 to 16,000 pounds for mercury cells. Methods of removing chlorine from these streams are summarized in the next section, Control of Emissions.

The venting of returned tank cars yields about 450 pounds of chlorine per 55-ton tank car. In addition, the handling and loading of shipping containers generates an average of 1,700 pounds per 100 tons of chlorine liquefied. These quantities are from venting and loading operations without controls. Most of this gas is returned to the liquefaction system or controlled by means of scrubbing systems.

Carbon dioxide is generated in mercury-cell and diaphragm-cell chlorine plants. Tests of blow gas in a diaphragm-cell plant before treatment showed CO_2 gas in amounts of 3,100 to 4,480 pounds per 100 tons of chlorine produced. Carbon monoxide in the cell gas amounts to about 0.02 percent by volume.

Other emissions include mercury vapor from mercury-cathode cells; chlorine from compressor seals, header seals, and storage tank vents; and air blowing of depleted brine in mercury-cell plants.

Chlorine emissions from the Downs cell are of the order noted from mercury and diaphragm cells. The Downs cell itself is a source of metal oxide fume during startup.

Emissions from the lime-soda process consist of soda particulate from lime-reburning kilns from the handling of soda-ash before solution. Carbon dioxide is also emitted from the lime kiln. Particulate loss from lime-reburning kilns has been measured at 980 to 1,880 pounds per day for a 120-ton-per-day lime kiln at collection efficiencies of 86 to 97 percent. Other tests have yielded a figure of 335 to 1,346 pounds per day from a 290-ton-per-day kiln at 98 to 98.7 percent control efficiency.

Carbon dioxide is evolved from lime burning in stoichiometric quantities of 0.785 ton of CO_2 per ton of lime.

CONTROL OF EMISSIONS

Chlorine emissions from chlor-alkali plants may be controlled by the following three general methods: (1) use of dilute gas streams in other plant processes, (2) neutralization in alkaline scrubbers, and (3) recovery of chlorine from effluent gas streams.

Waste chlorine can be used to synthesize chlorinated hydrocarbons, bleach, hydrochloric acid, and sulfur monochloride. It has also been used for chlorination of plant cooling water.

When plant effluent gas streams contain less than 1 percent chlorine, recovery of chlorine is not economical. Current practice involves scrubbing with alkaline solutions to neutralize chlorine-producing hypochlorites. The scrubbing is accomplished by using sodium or calcium hydroxide solution in packed, plate, or spray towers. Efficiencies of more than 99 percent have been obtained.

Waste gas streams, generally containing more than 10 percent chlorine, lend themselves to the recovery of chlorine by absorption of the gas in water or a carbon tetrachloride solution through the use of spray or packed towers. Chlorine is subsequently stripped from the absorbing medium in a distillation tower, thus regenerating the absorption medium for recycle. Absorption by sulfur monochloride is also used, though less commonly. Sulfur monochloride contacts gaseous chlorine to form sulfur dichloride, from which chlorine is then distilled. Some absorption systems employing stannic chloride, ethylene dichloride, etc., although patented, are not commercially significant. Chlorine can also be removed from effluent gases by adsorption onto silica gel or activated carbon. These methods are not used commercially either.

EMISSION GUIDELINES

Inert gases purged from chlorine plant operations contain substantial quantities of chlorine gas and constitute the largest potential source of chlorine emissions. In many cases, the chlorine can be recovered for use either by diverting the inert gas that contains it to other plant processes or by absorbing the chlorine from the gas and subsequently regenerating it. In other cases, chlorine in the inert gases can be neutralized by caustic soda or lime.

A properly designed and operated water scrubber may be expected to operate at efficiencies of 97 percent or greater, with exit-stream chlorine concentrations of less than 0.5 percent, representing a chlorine loss of less than 100 pounds per 100 tons of chlorine produced. Chlorine recovery efficiencies with carbon tetrachloride absorbers are reputed to be essentially complete, although no quantitative data on this type of system are available for either chlorine or carbon tetrachloride emissions.

Alkaline scrubbers that react caustic or lime with dilute concentrations of chlorine in inert gas streams are very effective, with an absorption efficiency approaching 99.9 percent for a well-operated unit. Exit-stream chlorine concentrations can be expected to be less than 10 ppm.

Carbon dioxide is generated in chlorine cells by oxidation of the graphite anodes. Approximately 2,000 pounds per 100 tons of chlorine are produced in mercury-cell plants and 4,000 pounds per 100 tons of chlorine in diaphragm-cell plants. This may comprise 15 percent or more of the blow gas emitted to the atmosphere. Carbon monoxide is also produced from graphite electrodes and may amount to 0.4 percent of the blow gas by volume.

Losses of mercury in the form of vapor from mercury-cell plants are small and proper building ventilation reduces mercury concentrations inside to negligible levels.

Submerged pumps, if used for transfer of liquid chlorine, eliminate the loss of chlorine attendant with air padding. To minimize emergency venting when maintenance and repairs are required for such pumps, small pump tanks should be used that can be isolated from storage tanks during servicing.

CHLOR-AKALI INDUSTRY

HISTORICAL BACKGROUND

Karl Wilhelm Scheele, a Swedish chemist, discovered chlorine in 1774 while working on the analysis of manganese dioxide. Although chlorine was not generally believed to be an element until 40 years after its discovery, Sir Humphrey Davy, in 1810, substantially verified Scheele's theory that chlorine was "dephlogisticated marine acid" and named the chemical "chlorine." It was not until 1815, through extensive work by Joseph Louis Gay-Lussac, that chlorine was generally accepted as an element. Chlorine gas was first used for bleaching in 1785, but it did not find acceptance because of its corrosive action on metals and the discomfort it caused workmen. Chlorine water was next tried and, in 1789, chlorine was absorbed in potassium hydroxide to form a potassium hypochlorite solution which proved to be successful as a bleaching agent. The potassium hydroxide was replaced by milk of lime in 1798, by G. Tennent of Glasgow, who was granted a patent that year for his new bleaching solution. It achieved immediate success in bleaching linen and cotton and, soon after, in bleaching paper.

Chlorine was first produced commercially by the Deacon process, in which hydrochloric acid is oxidized by air to chlorine using either MnO_2 or Cu_2CO_2 as a catalyst. The overall reaction of that process is:

$$4\,HCl + O_2 \longrightarrow 2Cl_2 + 2H_2O$$

Commercial production of chlorine in the United States was started in 1892 at Rumford Falls, Maine, where the Electro-Chemical Company developed a bell-jar-type electrolytic cell.[1] The plant was moved to Berlin, New Hampshire, in 1898 and until its recent shutdown was operated by the Brown Paper Company. Other companies–S. D. Warren, Olin, and Dow–followed in quick succession. Roberts Chemical Company started producing electrolytic chlorine in 1901, followed by the Developing and Funding Company in 1905. Other pioneer manufacturers were Pennsylvania Salt Manufacturing Company in 1903, Warner-Klipstein Company in 1915, and pulp manufacturers, including the New York and Pennsylvania Company and the West Virginia Pulp and Paper Company.

One of the earliest uses of chlorine in the United States was in the manufacture of bleaching powder, which was produced by passing chlorine gas over beds of hydrated lime. The Niagara Alkali Company, Niagara Falls, New York, first liquefied chlorine gas in 1909.[2] This proved to be a turning point in the industry, so that by 1910 there were 11 plants in the United States producing liquid chlorine, with a total installed capacity of about 200 tons per day. By 1920 the capacity had increased to 600 tons per day; in 1940 the total installed capacity was nearly 2,000 tons per day and by the end of 1969 was in excess of 28,000 tons per day.

The original electrolytic chlorine cell was of bell-jar design. The development of diaphragm-type cells in the United States was favored by the existence of underground sodium chloride brine and the easy extraction of underground solid salt deposits as brine. Since the mercury-cathode or mercury-type cell requires solid salt for resaturation of the depleted brine from the cells, the growth of the industry in Europe, where salt was generally more available in solid form, favored the mercury cell.

A recent trend toward mercury cells in the United States is the result of increased demands for high-purity caustic, which can be produced directly in this type of cell. Most of the diaphragm-cell caustic soda is sold as standard grade containing about 1 percent sodium chloride. Processes have been developed, however, to reduce the salt content to meet the specifications required for rayon manufacture and for other special uses.

GROWTH OF INDUSTRY

Since the start of the chlor-alkali industry in the United States at the turn of the century, the growth of the electrolytic chlor-alkali industry has been rapid. Although chlorine was first produced chemically, production by chemical means is now less than 0.5 percent of the total production. Within the last 35 years, production of chlorine in the United States has increased 25-fold. Production at the beginning of 1970 was at a rate in excess of 30,000 tons per day with an anticipated growth in 1970 of about 6 percent. Nearly 50 percent of all chlorine produced in this country is liquefied.

Electrolytic production of chlorine from sodium chloride brine will theoretically release 1.13 tons of sodium hydroxide per ton of chlorine produced. The market growth rate for caustic soda has not kept pace, however, with the increased demands for chlorine. Consequently, as electrolytic chlorine production has increased, caustic soda produced by chemical means has been replaced by caustic soda produced electrolytically. There were no known lime-soda plants in operation as of January 1970. Figure 1 shows the growth of chlorine production in the United States by years and the amount that has been produced with diaphragm and with mercury cells.

There were approximately 70 chlorine establishments in the United States as of January 1970, most of which are located in the eastern part of the country because of the availability of salt and a proximity to skilled labor and markets. Plants west of the Rocky Mountains are concentrated in the Northwest in proximity to paper mills. Most of the chlorine plants in the United States have a captive market for all or part of their chlorine.

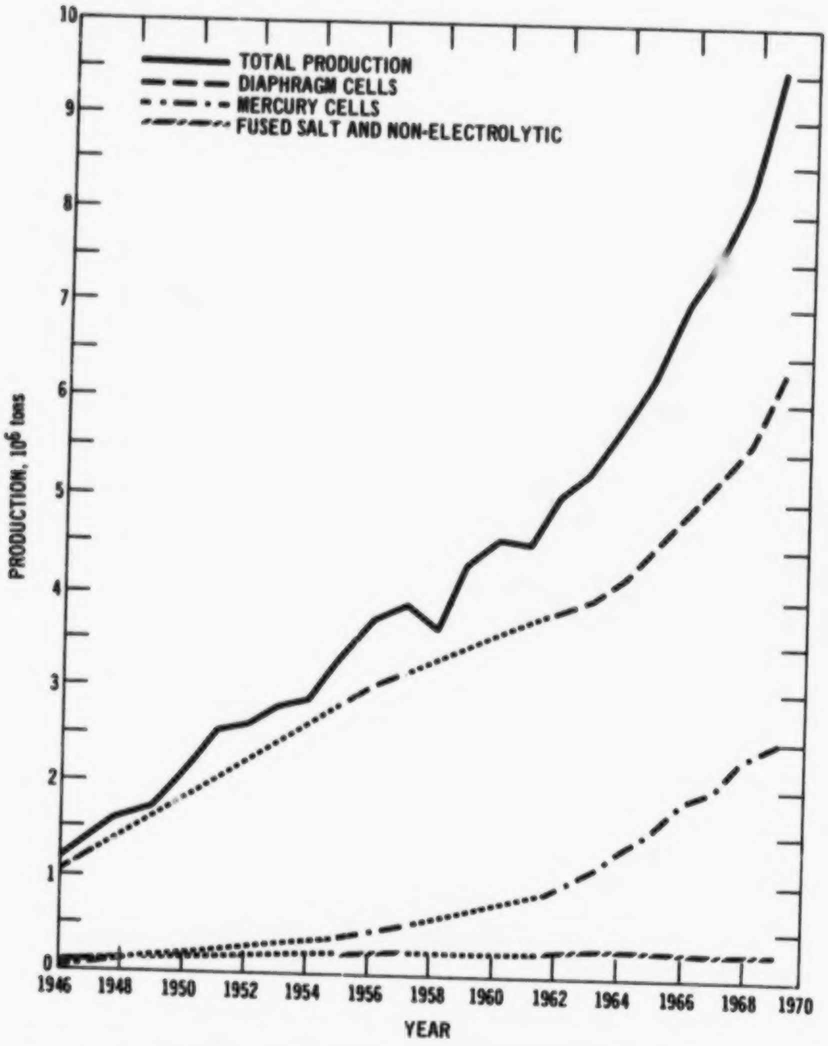

Figure 1. Chlorine production in United States by cell type.[3] (Percentage of production by respective cell type not available for 1947 to 1955 or 1957 to 1961.)

Figure 2 shows caustic soda production by years and the amount produced by the electrolytic and lime-soda processes. The distribution by use of chlorine and caustic soda is summarized in Tables 1 and 2, respectively.

FUTURE TRENDS

Chlorine, caustic, and related products are expected to maintain a healthy growth pattern for a number of years ahead. Estimated rate of growth for the next 5 years or so is 6 percent per year for chlorine, 5.5 for caustic soda, and 3 for caustic potash. No major technological changes are anticipated in the next 10 years that will seriously affect either the total demand for these products or their relationship to each other.

In an attempt to compensate for the slower growth of demand for caustic compared with that for chlorine, many studies have been conducted on ways to produce chlorine without producing caustic. Efforts have also been made to

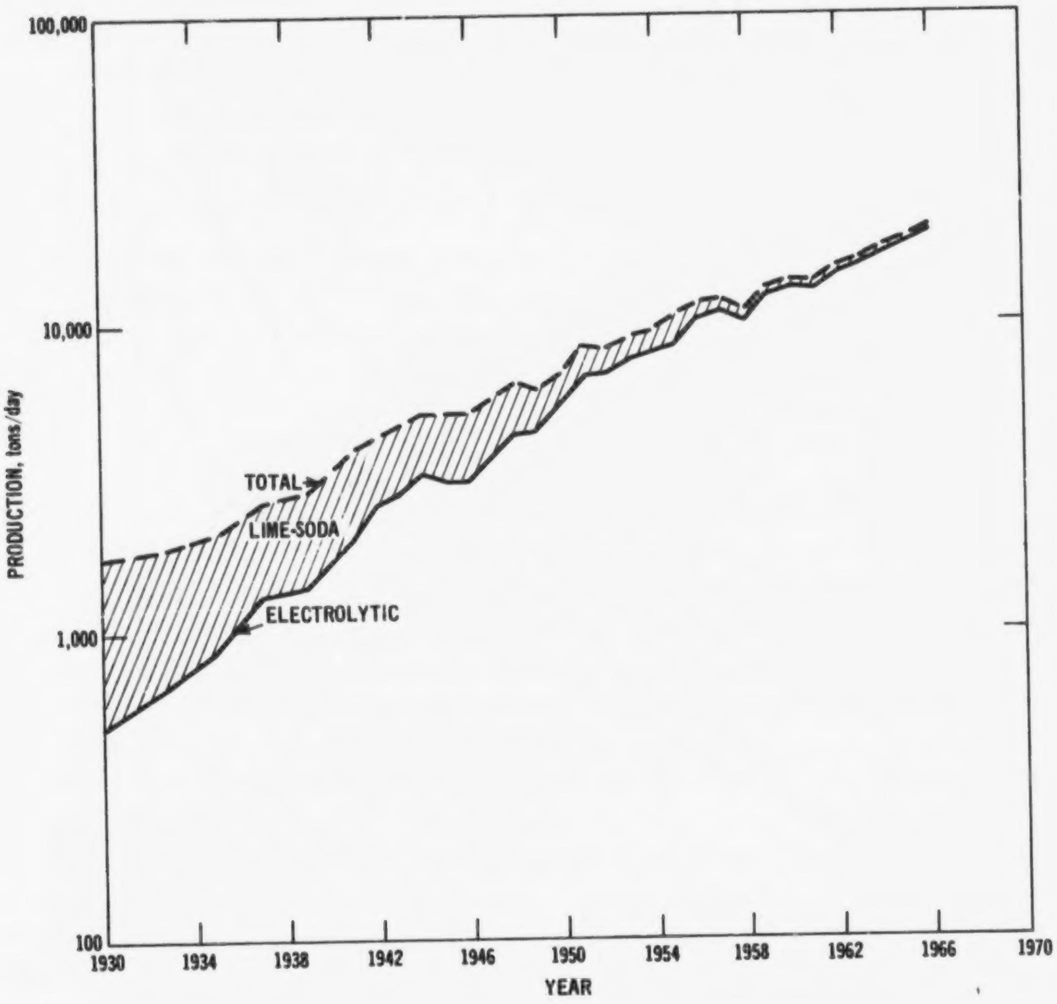

Figure 2. Caustic soda production in United States.[4]

diversify and expand the uses of caustic. None of these efforts have been particularly successful. The electrolytic processing of sodium and magnesium in molten-salt cells produces chlorine without caustic soda, but the market requirements for these metals have not been sufficient to correct the imbalance in demands for chlorine and caustic. An electrolytic process to decompose by-product hydrochloric acid is available and may be economically justified whenever excess acid might otherwise constitute a disposal problem.

Table 1. ESTIMATED 1969 END-USE DISTRIBUTION OF CHLORINE[3]

End use	Percent of total
Organic chemicals	64.5
Pulp and paper	11.6
Inorganic chemicals	10.7
Water treatment	3.6
Miscellaneous	9.6
Total	100.0

Table 2. ESTIMATED 1969 END-USE DISTRIBUTION OF CAUSTIC SODA[3]

End use	Percent of total
Chemicals	42.5
Pulp and paper	13.6
Rayon	5.4
Aluminum	7.4
Textiles	3.9
Petroleum	3.8
Soap and detergents	4.8
Cellophane	2.1
Export	1.3
Miscellaneous	15.2
Total	100.0

CHLORINE AND CAUSTIC MANUFACTURE BY DIAPHRAGM AND MERCURY CELLS

PROCESS DESCRIPTION

As of January 1970, more than 97 percent of the chlorine and nearly all of the caustic produced in the United States were made by electrolytic cells of the diaphragm or mercury type. Although diaphragm cells account for slightly over two-thirds of the present production, about half the plants under construction in 1968 had mercury cells. This reflects an increased demand for the higher-purity caustic produced by mercury cells.

Chlorine and caustic are produced concurrently in both types of cells. Both types use the same basic raw materials, employ electrolysis, and are similar in the generation and treatment of waste gases; however, there are differences in the design and operation of and emissions from the two types of cells. The raw materials and brine treatment used, the design and operation of the cells, and the sources and emissions of air pollutants for both types are described in subsequent sections of this report.

Raw Materials

An aqueous solution of sodium chloride is usually employed as the electrolyte in electrolytic cells. Other metal chlorides such as potassium chloride are also used, but to a much smaller extent. Generally, sodium chloride is obtained either from brine wells, underground deposits of solid salt, or ocean water. Salt derived from these sources is 95 percent or more pure and contains small amounts of calcium (usually as calcium sulfate), magnesium, iron, and clay. Before its use, raw brine is treated to remove some of the impurities.

Salt used in mercury plants requires more extensive treatment to produce a higher purity brine than that necessary for diaphragm cells. The high-purity salt produced from caustic evaporation usually practiced in diaphragm-cell plants can be used as raw material for mercury cells.* In some mercury-cell plants

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*Based on the assumptions of approximately 52 percent decomposition of brine feed for diaphragm-cell operation and 20 percent of the salt return required for resaturation, including salt losses, a 100-ton-per-day diaphragm-cell plant would be able to produce sufficient purified solid salt beyond its own needs to supply a 75-ton-per-day mercury-cell plant.

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depleted brine from the cells is resaturated by pumping it to underground salt deposits that serve as subsurface resaturators.

Brine Treatment

Diaphragm Cells

Since calcium and magnesium salts tend to build up on diaphragms, raw brine is treated with soda ash and caustic and is then filtered to reduce these elements to reasonable levels. Sulfates must also be kept under control since sulfate ions decrease graphite life. The practice of providing for the rapid solution of salt with prompt removal of the brine leaves much of the calcium sulfate undissolved and thus minimizes brine purification costs. Recycled brine may also be high in sulfates. In plants where salt costs are low, sulfates in the feed brine are usually controlled by discarding or purging high-sulfate brine returned from the caustic evaporation process. This brine, or "transfer liquor," as well as the first warm-water wash of the returned salt, may contain about 175 to 200 pounds of sodium sulfate per 1,000 pounds of sodium chloride. Where salt costs are high, the first warm-water wash of the returned salt, or a portion of the transfer liquor, may be refrigerated to crystallize sodium sulfate as the decahydrate ($Na_2SO_4 \cdot 10H_2O$), which is then discarded.

Mercury Cells

In most mercury-cell plants about 10 to 15 percent of the sodium chloride is decomposed as the brine passes through the cell. Depleted brine must usually be dechlorinated before recycle. Depleted brine leaving the electrolyzer is first sent to a storage tank, is usually acidified with hydrochloric acid, and is then reacted with hypochlorite in the brine, forming some free chlorine. The brine is then subjected to vacuum or is air blown, or both, to remove most of the chlorine. This gas is usually piped to the cell header. When high vacuum is used, the air-blowing step is sometimes omitted. Brine is dechlorinated before resaturation for the following reasons:

1. Control of iron removal is difficult in the presence of hypochlorite ion.
2. Hypochlorous acid, if not removed, will be converted to chlorate, resulting in rapid graphite attack.
3. Workmen are caused less discomfort by this process.

Dechlorinated brine contains about 260 to 280 grams of NaCl per liter and is usually at a temperature of about 50 to 80° C. It is made neutral or alkaline before resaturation.

After dechlorination, the brine is resaturated. Some operators prefer to purchase or manufacture a "mercury-cell grade" of salt for use in resaturating the brine because no further purification is then needed. Others prefer to use a lower grade of salt. The brine must then be purified to remove iron and other metals since small traces of vanadium, chromium, and molybdenum deposit out, form a film on the mercury, and thereby increase the cathode overvoltage. This increases the breakdown of the amalgam with an increase of hydrogen in the chlorine. These impurities are usually removed by adding caustic soda, soda ash, and/or barium carbonate or barium chloride, followed by settling, filtration, or both, to remove precipitated metallic compounds.

Cell Description and Operation

Diaphragm Cells

Diaphragm cells consist essentially of three parts: the anode compartment, the cathode compartment, and the diaphragm separating the two. This comprises a unit cell. During the past 10 years all new diaphragm cells have been of two basic types. One type consists of a filter press or box structure that contains as many as 50 unit cells. The cells are arranged in the building so that a maximum of four such assemblies may be operated in series, making as many as 200 unit cells in the series.

The second type consists of a single-unit cell. This cell is also connected in series to feed into common chlorine and hydrogen collection systems. Both types of cells have vertical graphite anodes, steel screen cathodes, and deposited asbestos diaphragms.

The Hooker cell (Figures 3 and 4) is an example of the single-unit cell type. The anode section consists of a concrete bottom holding an assembly of closely spaced graphite blades cast in lead. Extending through the side of the bottom are copper bus bars to conduct current into the lead. The cathode section rests on the concrete bottom and is constructed of steel plate with fingers of wire screen coated on the anode side with an asbestos diaphragm. A concrete top is sealed to the cathode section.

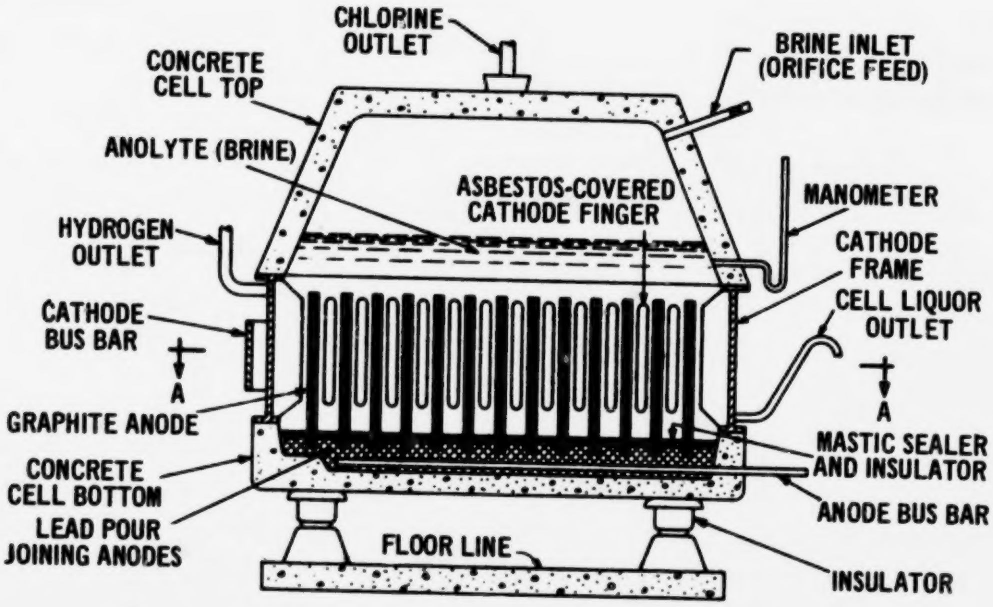

CHLORINE OUTLET
CONCRETE CELL TOP
BRINE INLET (ORIFICE FEED)
ANOLYTE (BRINE)
ASBESTOS-COVERED CATHODE FINGER
MANOMETER
HYDROGEN OUTLET
CATHODE FRAME
CATHODE BUS BAR
CELL LIQUOR OUTLET
+
A
+
A
GRAPHITE ANODE
MASTIC SEALER AND INSULATOR
CONCRETE CELL BOTTOM
ANODE BUS BAR
LEAD POUR JOINING ANODES
FLOOR LINE
INSULATOR

Figure 3. Vertical section through typical diaphragm cell (cells connected electrically in series).

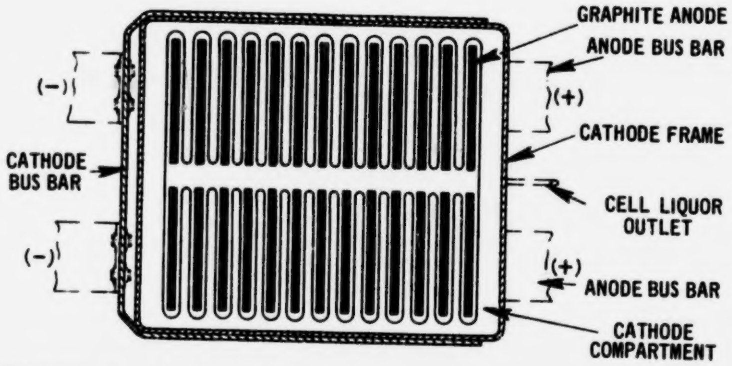


Figure 4. Horizontal section through typical diaphragm cell (cross section at A-A (Figure 3)) to indicate arrangement of anodes and cathode fingers.

Electrical connections from one cell to the next are made with L-shaped copper connector bars. Cells can be removed from this circuit individually for renewal by using a portable jumper switch. The jumper is applied without the interruption of current to the circuit.

The Dow dipolar cell is the only type of filter-press cell now in use for chlorine production. Current passes through approximately 50 cells in series without electrical connectors between successive cells. Concrete frames are pressed together, with each unit connected electrically to the next cell within the frame. Graphite plates form a tight, vertical partition across the concrete frame, and graphite anode plates are set into this portion in vertical rows. The cathode, which is a steel wire screen bolted to the concrete frame, has vertical, hollow fins spaced to form pockets between the rows of anode plates. Asbestos fiber is deposited on the side facing the anodes.

Figure 5 is a flow diagram of a typical chlor-alkali diaphragm-cell installation. The overall reaction effected by the electrical current when sodium chloride brine is used is as follows:

$$\begin{array}{c} 2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2 \\ \text{(sodium chloride + water} \longrightarrow \text{caustic soda + chlorine + hydrogen)} \end{array} \qquad (2)$$

Potassium chloride may be used in place of sodium chloride in diaphragm cells, in which case potassium hydroxide is produced. Market demand for potassium hydroxide is very small, however, compared with that for caustic soda.

Anodic reaction– In most diaphragm cells, hot, purified, saturated brine is fed continuously to the anode compartment. Brine in the anode compartment, known as anolyte, is in direct contact with graphite anodes. Chlorine gas is evolved at the anode and leaves the cell saturated with water vapor. This gas is cooled in direct or indirect water coolers to condense most of the water and is then dried in direct-contact sulfuric acid drying towers. Some plants employ mist eliminators after the coolers and use sulfuric acid towers to remove liquid,

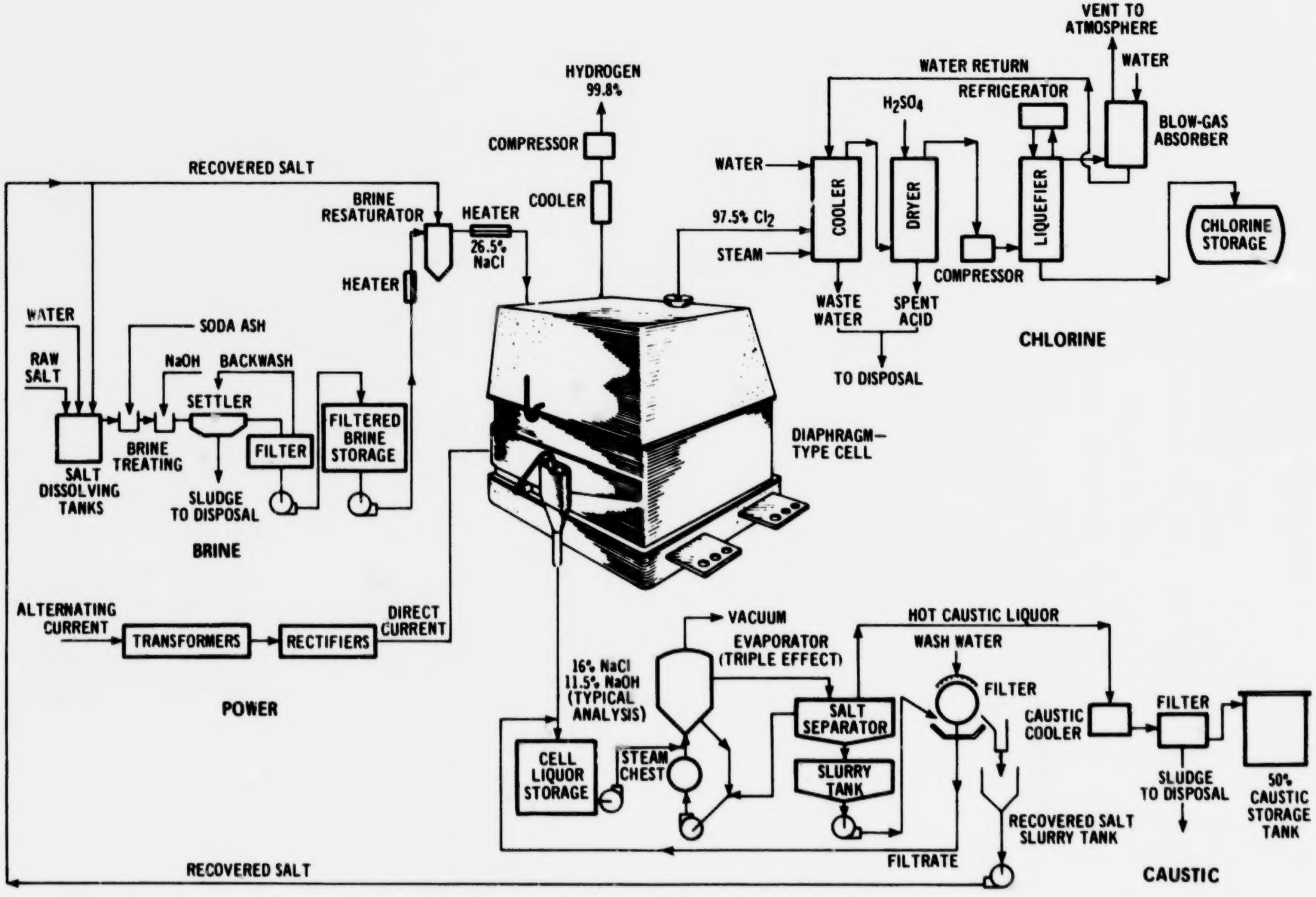

VENT TO ATMOSPHERE
WATER
WATER RETURN
REFRIGERATOR
BLOW-GAS ABSORBER
HYDROGEN 99.8%
COMPRESSOR
COOLER
H_2SO_4
WATER
97.5% Cl_2
STEAM
COOLER
DRYER
LIQUEFIER
CHLORINE STORAGE
COMPRESSOR
WASTE WATER
SPENT ACID
TO DISPOSAL
CHLORINE
RECOVERED SALT
BRINE RESATURATOR
HEATER
26.5% NaCl
HEATER
WATER
RAW SALT
SODA ASH
NaOH
BACKWASH
SETTLER
FILTERED BRINE STORAGE
FILTER
SALT DISSOLVING TANKS
BRINE TREATING
SLUDGE TO DISPOSAL
BRINE
DIAPHRAGM—TYPE CELL
ALTERNATING CURRENT
TRANSFORMERS
RECTIFIERS
DIRECT CURRENT
POWER
VACUUM
EVAPORATOR (TRIPLE EFFECT)
HOT CAUSTIC LIQUOR
WASH WATER
FILTER
16% NaCl
11.5% NaOH
(TYPICAL ANALYSIS)
SALT SEPARATOR
SLURRY TANK
CELL LIQUOR STORAGE
STEAM CHEST
CAUSTIC COOLER
FILTER
SLUDGE TO DISPOSAL
50% CAUSTIC STORAGE TANK
RECOVERED SALT SLURRY TANK
FILTRATE
RECOVERED SALT
CAUSTIC

Figure 5. Flow diagram of a typical diaphragm-cell chlor-alkali installation.

condensable vapors, and solid impurities.[5] The chlorine is compressed and all or part of it may be further cooled by refrigeration to produce liquid chlorine. Chlorine is shipped as a liquefied gas under pressure in tank cars, tank trucks, barges, 1-ton containers, or cylinders. Chlorine gas is also shipped by pipeline over distances of several miles from one plant to another.

Small amounts of oxygen, carbon dioxide, carbon monoxide, and hydrogen are produced within the cells because of side reactions (current efficiency is normally 95 to 96 percent). These gases, along with a small amount of air leakage into the chlorine system, usually represent 4 to 6 percent by volume of the main chlorine gas stream. A typical chlorine-cell gas analysis is given in Table 3.

Table 3. TYPICAL DIAPHRAGM-CELL GAS ANALYSIS

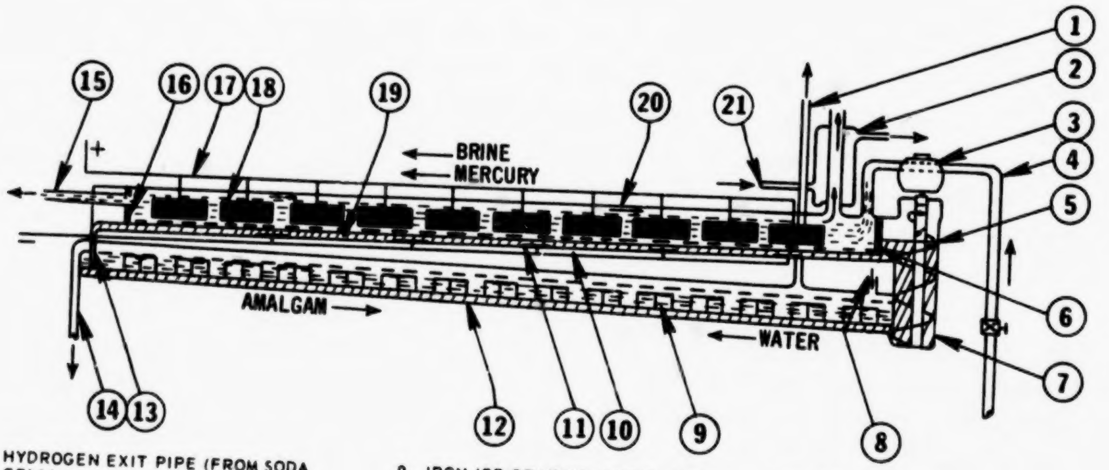
Component	Volume, %
Cl_2	96.28
CO_2	1.61
N_2	1.27
O_2	0.66
H_2	0.12
CO	0.02

Cathodic reaction–The anolyte passes from the anode section into the cathode section by gravity flow through a porous asbestos diaphragm. The liquor leaving the cathode compartment contains about 11 percent caustic and 15 percent salt. It is sent to evaporators where it is concentrated to 50 percent or, sometimes, to 73 percent caustic. During the evaporation step excess salt precipitates out. This salt is filtered, washed, and returned as a slurry to the brine system.

Mercury Cells

A mercury cell consists of two sections, the electrolyzer and the denuder. The electrolyzer has a chlorine outlet, graphite anodes, and a mercury cathode (Figure 6). It is generally constructed with a flat-bottomed steel trough in which mercury and brine flow uniformly. The anodes are usually horizontal graphite plates that hang on insulated rods from the top of the cell. The anodes are close and parallel to the mercury-brine interface, with a space of several millimeters between them that allows the chlorine to get to the outlet. Mercury cells generally have greater current-carrying capacity (100,000 to 200,000 amperes) than diaphragm cells (30,000 to 60,000 amperes).

The denuder is usually a steel duct mounted below or alongside the electrolyzer. It has a mercury-amalgam anode and iron or graphite cathodes. No electrical power is applied to the denuder. Design variations in mercury



1. HYDROGEN EXIT PIPE (FROM SODA CELL)
2. CHLORINE EXIT PIPE (FROM BRINE CELL)
3. ELECTRIC MOTOR DRIVING SCREW PUMP
4. BRINE FEED PIPE
5. ARCHIMEDEAN SCREW PUMP RAISING DENUDED MERCURY FROM SODA CELL TO BRINE CELL
6. BARRIER ACROSS BRINE CELL PERMITTING MERCURY TO FLOW BELOW IT AND PREVENTING BRINE FROM PASSING BACK INTO MERCURY PUMP
7. DENUDED MERCURY FROM SODA CELL
8. WATER FEED PIPE TO SODA CELL
9. IRON (OR GRAPHITE) GRIDS PROMOTING DECOMPOSITION OF SODIUM AMALGAM
10. ELECTRICAL CONNECTION TO PLATE IN BASE OF THE BRINE CELL (see 11)
11. ELECTRICAL CONTACT PLATE OVER WHICH MERCURY CATHODE FLOWS
12. SODIUM AMALGAM FLOWING ALONG SODA CELL
13. PIPE THROUGH WHICH AMALGAM PASSES FROM BRINE CELL TO SODA CELL
14. CAUSTIC LIQUOR EXIT PIPE
15. BRINE EXIT PIPE
16. BARRIER ACROSS BRINE CELL PERMITTING AMALGAM TO FLOW BELOW IT AND PREVENTING BRINE FROM PASSING INTO SODA CELL
17. ELECTRICAL CONNECTION TO ANODES
18. ANODE BLOCK
19. MERCURY CATHODE
20. CHLORINE GAS PASSING ALONG BRINE CELL IN SPACE BETWEEN CELL COVER AND BRINE
21. WATER FEED PIPE TO COOLING JACKET OF CHLORINE EXIT PIPE

Figure 6. Typical mercury-cathode cell.

cells include cathode and anode orientation for both the electrolyzer and denuder, type of mercury flow, and construction of the cell parts.

The reaction in each section of the cell can be shown as follows: In the electrolyzer:

$$\mathrm{NaCl + Hg \longrightarrow Na(Hg) + 1/2\ Cl_2} \tag{3}$$

In the denuder:

$$\mathrm{Na(Hg) + H_2O \longrightarrow NaOh + 1/2\ H_2 + Hg} \tag{4}$$

The net reaction is the same as that for diaphragm cells:

$$\begin{gathered}\mathrm{2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2} \\ \text{(sodium chloride + water} \longrightarrow \text{caustic soda + chlorine + hydrogen)}\end{gathered} \tag{5}$$

Electrolyzer reaction–Brine and liquid-mercury cathode are fed continuously into the electrolyzer section. Chlorine evolves from the surface of the anodes and passes out of an opening at the top of the cell. The chlorine is cooled, dried, and liquefied in the same manner as that from diaphragm cells.

Denuder reaction–On electrolysis, the sodium forms an amalgam with mercury, the mercury containing about 0.1 to 0.3 percent sodium. The amalgam flows to a denuder where it becomes the anode to a short-circuited iron or graphite cathode. Hydrogen, caustic, and mercury are the products when the amalgam reacts with water.

The hydrogen gas is cooled and compressed in a manner similar to that used with diaphragm cells. Hydrogen from mercury cells contains traces of mercury vapor, most of which is removed in a direct-contact scrubber or in a condenser so that the resulting gas is approximately 99.9 percent H_2 on a dry basis and contains 20 to 30 milligrams of mercury per cubic meter.[6] In some cases the gas is further purified by deep cooling and by filtering through activated adsorbents to remove the remaining traces of mercury.

Caustic produced in a mercury cell is unusually pure because there is no direct connection between the brine solution in the electrolyzer and the caustic solution in the denuder. Moreover, a mercury cell usually produces 50 percent caustic liquor in comparison with the 11 percent caustic produced in a diaphragm cell. This pure, concentrated caustic normally requires no further processing other than filtration.

Investment and operating costs are higher for mercury cells because of the cost of mercury, mercury losses, and higher energy requirements (15 percent) per ton of product.

SOURCES AND QUANTITIES OF EMISSIONS

Atmospheric emissions of chlorine, carbon dioxide, carbon monoxide, and hydrogen occur from diaphragm- and mercury-cell plants in amounts that depend largely upon plant design and operation. If liquid chlorine is not produced (as in a paper mill plant), the plant will have no blow gas resulting from liquefaction and will have, therefore, no chlorine emissions from this source. Where liquid chlorine is produced, emissions vary according to the waste treatment system employed and the chlorine content of the blow gas.

Chlorine Emissions

Blow Gas

When a chlorine-cell gas such as that described in Table 3 is compressed and cooled to produce liquid chlorine, noncondensable gases saturated with chlorine vapor are produced at the discharge of the condenser. These gases are commonly called blow gas, sniff gas, or tail gas. The amount of chlorine emitted to the atmosphere from blow gas varies with operating conditions and the type of recovery equipment through which the stream is processed. It varies with plant capacity, concentration of chlorine in the blow gas, percentage of inerts in the cell gas, and according to whether air is injected before the chlorine condenser to prevent an explosive mixture in the vent gas (Appendix A).

Table 4 shows ranges of concentrations and the amounts of chlorine that may be emitted if these emissions are uncontrolled and when various types of scrubbers are used to remove chlorine.

Table 4. CHLORINE EMISSIONS FROM LIQUEFACTION BLOW GASES IN DIAPHRAGM- AND MERCURY-CELL PLANTS

Type of control	Chlorine concentrations in exhaust, vol %	Emission factor, 1b chlorine/100 tons chlorine liquefied
None	20 to 50	2,000 to 16,000
Water absorber	0.1 to 4.5	25 to 1,090
Caustic or lime scrubber	0.0001	1

A typical range for the diaphragm cells is 2,000 to 10,000 pounds of chlorine in the blow gas per 100 tons liquefied. Mercury-cell installations usually require more air dilution because more hydrogen is contained in the cell gas. The usual range of chlorine in the blow gas is 4,000 to 16,000 pounds of chlorine per 100 tons of chlorine liquefied.

It is common practice to operate at condensing pressures and temperatures that represent an economic optimum. When there is no use for chlorine in the blow gas and chlorine must be neutralized, it becomes economical to condense at higher pressures or lower temperatures, or both, to reduce the chlorine in the blow gas. If useful by-products can be made, or if the chlorine in the blow gas is recycled or recovered in some other manner, it will usually be more economical to allow the percentage chlorine in the blow gas to increase in lieu of operating at relatively high pressures or low temperatures, or both.

The high operating costs encountered when chlorine in the blow gas must be neutralized and discarded have directed considerable attention to methods of recycle or recovery. This is particularly true for gas streams with large concentrations of carbon dioxide since this compound also reacts with alkali.

Abnormal operating conditions that increase the quantities of chlorine in the blow gas are given below.

Operating above rated capacity–Cell manufacturers specify for a particular cell an upper current limit or cell load that determines the rate of chlorine, caustic, and hydrogen production. As technical and operating improvements have been made, cell ratings for both new and existing cells have increased. If existing chlorine-condensing facilities are inadequate for the expanded plant production resulting from such improvements, the percentage of chlorine in the blow gas will increase and positive pressure may occur in the cell headers, resulting in chlorine emissions in the cell room.

Startup and shutdown–During chlorine plant startup, air is present in chlorine lines and equipment and liquefaction efficiencies are low, so that large amounts of blow gas are generated. A new cell circuit may require 8 to 24 hours to attain steady operating conditions at full load. Normally when a cell circuit is started up, every effort is made to maintain continuous operation; at times, however, entire circuits may be shut down for major repairs or for economic reasons. To minimize the excess air in the chlorine system at startup, liquid chlorine is frequently evaporated into the chlorine headers.

Vents from Returned Tank Cars, Ton Containers, and Cylinders

Occasionally water and other liquids are present in returned tank cars. In order to ensure an empty and clean car before reloading, it is common practice to apply suction to returned tank cars, as well as to cylinders and ton containers, to remove any liquid chlorine remaining in the vessel before inspection and cleaning. The amount of chlorine thus removed varies considerably but averages about 450 pounds for a 55-ton tank car.[3] The recovered chlorine is usually sent to the chlorine-handling system although some plants send the chlorine to a caustic scrubber to avoid upsetting their cell operation.

Vents from Storage Tanks, Process Transfer Tanks, and Tank Cars During Handling and Loading of Liquid Chlorine

A common method of transferring chlorine involves the use of air padding. After the transfer it is necessary to vent the air, which now contains a relatively small concentration of chlorine, because the transfer is normally completed before equilibrium conditions can be reached. The amount of chlorine in the vented air varies considerably and is greater at higher temperatures. It depends also upon the shape of the vessel, the time required for transfer, and the number of transfers made.

Quantities of chlorine are flushed out with the padding air during the loading of shipping containers with liquid chlorine. Data from 19 plants, given in response to a questionnaire for this study, show that the chlorine flushed out varied from 110 to 6,000 pounds per 100 tons of chlorine liquefied, with an average of 1,700 pounds. In all cases except two, chlorine removed during tank-car loading operations was transferred to other plant uses, returned to the process, or treated in a scrubber. In the two exceptions, the scrubber collection was not complete, and 10 to 140 pounds, respectively, of chlorine were vented per day. This represents a chlorine emission rate of 7.2 and 100.8 pounds of chlorine, respectively, per 100 tons of chlorine liquefied.

In many newer plants, submerged pumps are used for the transfer of liquid chlorine. Although pumps eliminate the loss of chlorine attendant with air padding, emergency venting is necessary for pump repair and general maintenance. These emergency vents are usually connected to a caustic scrubber. It is good practice to use small pump tanks that can be isolated from large storage tanks for servicing. This practice greatly reduces emissions during pump repair.

Another method of transfer is to apply suction on the receiver or vessel to which a transfer is to be made and connect the discharge from the compressor to the vessel containing the chlorine that is to be transferred. This is somewhat similar to transfer by means of air, except that neither tank requires any venting.

Water Removal from Chlorine Gas

Chlorine gas is normally cooled to condense water vapor and then is further dried in concentrated-sulfuric acid scrubbers. The loss of chlorine with the water that condenses from cell gas varies from 400 to 1,200 pounds of chlorine per 100 tons liquefied, depending on the type of cell, cell temperature, and location of drip connections in the chlorine gas system. Usually this condensate is flushed to the sewer. Care must be taken that such liquid streams are not discharged into a ditch or sewer that also receives strong acid wastes since this could result in the release of chlorine.[7] The sulfuric acid used for chlorine drying has a low solubility for chlorine, and loss of chlorine is, therefore, negligible when spent acid is discarded.

Emergency Vents

Chlorine seals and other sources of infrequent emissions are usually connected to an emergency scrubber, although in other cases these emissions are vented to the atmosphere. In either case, alarms and electrical tie-in connections are usually provided to permit prompt shutdown or changes in operating procedures to limit the duration of the emission.

Cell room chlorine header seals–Seals on chlorine headers, provided to prevent backpressure at the cells, are usually vented to the cell house or to the outside atmosphere. Although in an emergency they must handle the full capacity of the cells connected to the header, the seals blow infrequently and for short periods. In certain locations seals are piped to a lime or caustic scrubber designed to absorb all the cell chlorine produced.

Compressor seals–The shaft seals on liquid-seal chlorine compressors are usually piped so that a stream of sulfuric acid is fed into the compressor. Carbon-ring reciprocal compressors usually have a double stuffing box vented to a caustic scrubber or to the suction of the compressor. This effectively prevents emissions to the atmosphere.

Storage tanks–The tank vent line is usually connected to a disposal scrubber. The relief connection from the safety valves may be vented to the atmosphere or to an emergency scrubber.

Air Blowing of Depleted Brine in Mercury-Cell Plants

Recycled brine in mercury-cell plants is saturated with chlorine. This brine is usually vacuum-treated, air-blown, or both, to remove residual chlorine before resaturation. Concentrations of chlorine encountered in the vent gas are usually low* and economic recovery in a water or carbon tetrachloride absorber cannot be obtained. Consequently, such gases are normally used for in-plant purposes such as water chlorination, or they are sent to lime or caustic scrubbers for disposal or vented to the atmosphere. Although air blowing of depleted brine is common, it is by no means universal. For example, certain plants air-blow and re-treat only a 5 to 10 percent side-stream, and several plants dispense with this procedure entirely. The questionnaire responses of 11 plants indicating treatment of chlorine from brine blowing are given in Table 5.

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*From practical solubility data it can be shown that if brine is depleted by 10 percent in passing through the cell, approximately 1.5 percent of the chlorine produced is present in the depleted brine. If vacuum treatment of the depleted brine at 22.5 inches of Hg

Table 5. TREATMENT OF CHLORINE FROM AIR BLOWING OF DEPLETED BRINE[a]

Treatment	Number
Used for in-plant processes	7
Sent to scrubbers	3
Vented to atmosphere	1[b]

[a] Following vacuum degassing

[b] Fifty-six pounds of emissions per 100 tons chlorine produced. Note: Since about 540 pounds corresponds to 75 percent vacuum, 56 pounds residual indicates that an almost complete vacuum was used.

Mercury-Cell End Boxes

On certain mercury cells the discharge end box is constructed with a removable cover for servicing. End boxes are connected to a common suction header to prevent chlorine gas from entering the cell room when the covers of the end boxes are opened. Chlorine in the exhaust header is usually neutralized with lime or caustic.

Other Emissions

Carbon Dioxide

Carbon dioxide is generated in both diaphragm and mercury cells by oxidation of the graphite anodes.[8] In addition, carbonates present in the cold feed brine are decomposed during acidification, freeing carbon dioxide that is evolved as the electrolytic cell heats the feed brine to operating cell temperature. Typical cell gas contains 1 to 2 percent carbon dioxide.[9] Condensation of chlorine from the cell gas increases carbon dioxide concentrations in the blow gas to more than 15 percent.[10]

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suction (75 percent of full vacuum) is assumed, the vacuum treatment at equilibrium will recover 2,250 pounds (0.75 X 1.5 X 2,000) of chlorine per 100 tons produced. This corresponds to a reduction in chlorine content of hot brine from about 0.024 to 0.006 percent. Air blowing reduces the residual chlorine in the brine to 0.001 to 0.003 percent, depending on the quantity of air used. On the assumption that 0.02 gram per liter (0.00167 percent) chlorine remains in the depleted brine after air blowing, the air blow in this example will contain 0.27 ton (540 lb) of chlorine per 100 tons of chlorine produced, or about 500 ppm chlorine in the effluent airstream.

Analysis of one blow-gas stream before treatment reveals the carbon dioxide production rate shown in Table 6.

Table 6. CARBON DIOXIDE BEFORE BLOW-GAS TREATMENT IN DIAPHRAGM-CELL (PLANT 30)

Test	Inlet, lb CO_2/100 tons Cl_2 produced
1	3,100
2	4,280
3	4,340
4	4,480

Since less graphite is consumed in mercury cells,[11,12] carbon dioxide generated in mercury-cell plants is correspondingly lower and has been calculated to be about 2,000 pounds per 100 tons of chlorine produced. Like chlorine, carbon dioxide emissions to the atmosphere depend upon the blow-gas scrubber employed.

Carbon Monoxide

As shown in Table 3, carbon monoxide forms a small part of the inerts in the cell gas, amounting to 0.02 percent by volume and appearing in the same relative amounts in the blow gas. Assuming a 20-fold increase in carbon monoxide concentrations because of liquefaction of the chlorine, the carbon monoxide concentration in the blow gas would be 0.40 percent by volume.

Mercury

The use of mercury in mercury-cathode cells produces some mercury vapor, which is emitted during cell operations. The trend toward the use of higher-strength amalgams and, therefore, lower mercury requirements has minimized mercury-vapor emissions. Modern cells with steeper bottom slope, vertical decomposers, higher-strength amalgam, and increased current densities have reduced mercury inventory to slightly less than 90,000 pounds for a 100-ton-per-day chlorine plant, about half that required by older plants. With the newer cells, daily mercury losses have decreased from 0.6 pound to less than 0.3 pound per ton of installed daily chlorine capacity.[13] The usual range of mercury losses for typical plants in the United States has been given as 30 to 40 pounds per 100 tons of chlorine produced.[11] European sources[13] indicate that some 3 percent of the mercury lost is emitted to the surrounding atmosphere.

MINOR METHODS OF CHLORINE MANUFACTURE

FUSED-SALT CELL

Approximately 3 percent of the chlorine manufactured in this country is produced as a by-product of the Downs fused-salt process.

Process Description

Figure 7 is a flow diagram of the Downs fused-salt process. The process can be divided into four main steps: (1) preparation of dry sodium chloride and calcium chloride feed streams, (2) electrolysis, (3) treatment of gaseous chlorine by-products, and (4) purification of molten sodium.

In the salt preparation stage, a pure sodium chloride brine is obtained by dissolving raw salt in water and treating with sodium hydroxide and ferric and barium chlorides to remove impurities that would interfere with electrolysis. The pure brine is evaporated, filtered, and dried, and then fed to the Downs electrolytic cell along with dry calcium chloride.

Electrolysis of a molten salt bath occurs in the Downs cell (Figure 8) at a temperature of about 550° C, producing molten elemental sodium and gaseous chlorine.

The lower density sodium and the chlorine percolate separately through the molten salt bath to a submerged conical collection dome, where an outer annular ring and inner nickel dome remove the molten sodium and hot gaseous chlorine, respectively. A cell cover enclosing the collection dome reduces heat losses from the salt bath and minimizes contact with the atmosphere. An opening in the cover is provided for the salt feed. A vertical riser pipe, fitted with cooling coils at its upper end, continuously removes and cools the molten sodium so that dissolved metallic calcium precipitates and settles back into the bath. From the riser pipe, the crude sodium flows into a collector tank and then to a scale tank at 100° C, where a screen filter removes any remaining calcium and sodium impurities.

Sources and Quantities of Emissions

Chlorine emissions from the liquefaction and handling of Downs-cell chlorine are of the same magnitude as reported earlier for mercury- and diaphragm-cell processes. Chlorine blow-gas emissions may be prevented by:

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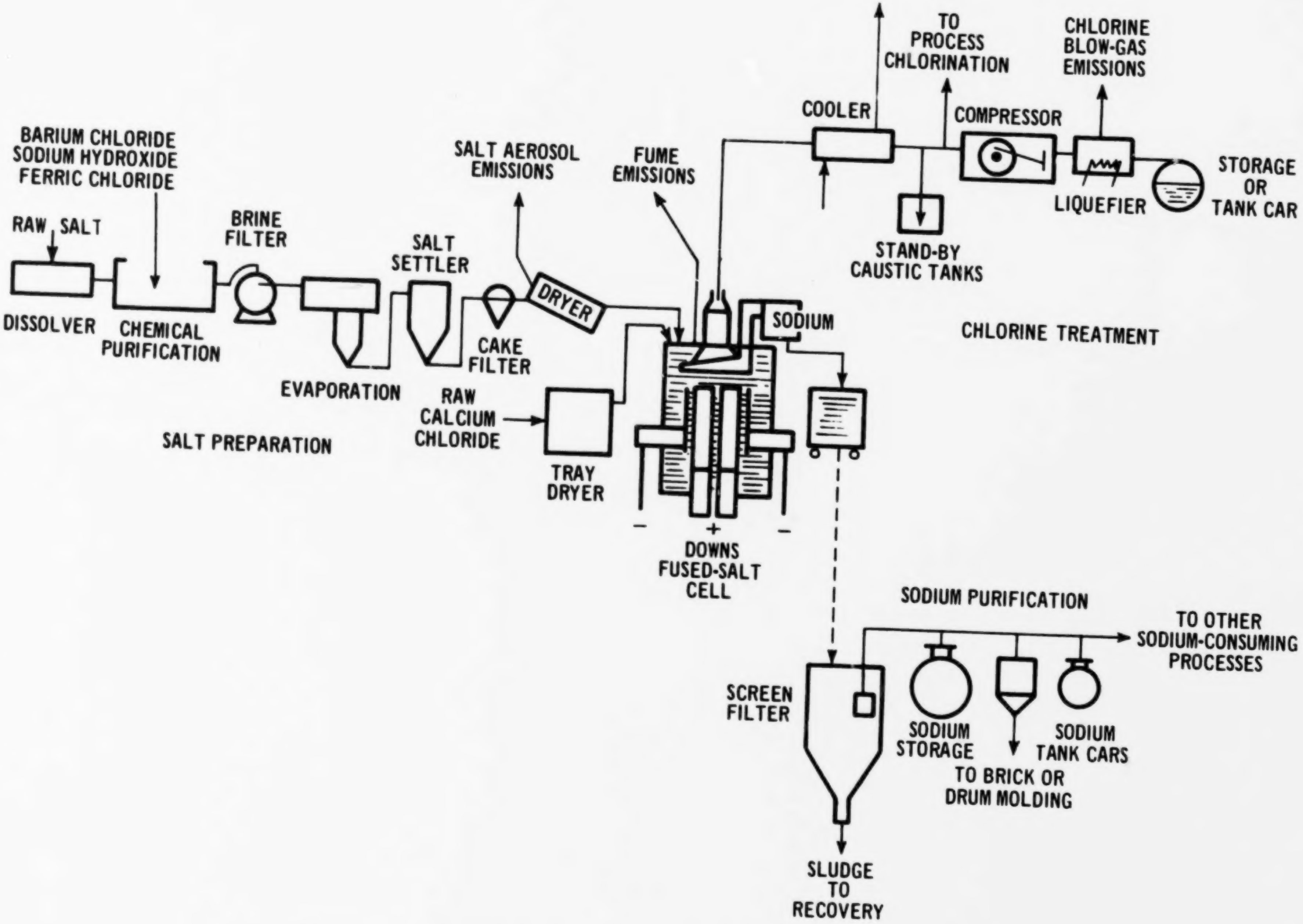
TO PROCESS CHLORINATION
CHLORINE BLOW-GAS EMISSIONS
COOLER
COMPRESSOR
LIQUEFIER
STORAGE OR TANK CAR
STAND-BY CAUSTIC TANKS
CHLORINE TREATMENT
BARIUM CHLORIDE
SODIUM HYDROXIDE
FERRIC CHLORIDE
RAW SALT
BRINE FILTER
SALT SETTLER
SALT AEROSOL EMISSIONS
FUME EMISSIONS
DRYER
SODIUM
DISSOLVER
CHEMICAL PURIFICATION
CAKE FILTER
EVAPORATION
RAW CALCIUM CHLORIDE
SALT PREPARATION
TRAY DRYER
– + –
DOWNS FUSED-SALT CELL
SODIUM PURIFICATION
TO OTHER SODIUM-CONSUMING PROCESSES
SCREEN FILTER
SODIUM STORAGE
SODIUM TANK CARS
TO BRICK OR DRUM MOLDING
SLUDGE TO RECOVERY

Figure 7. Manufacture of sodium by the Downs fused-salt process.

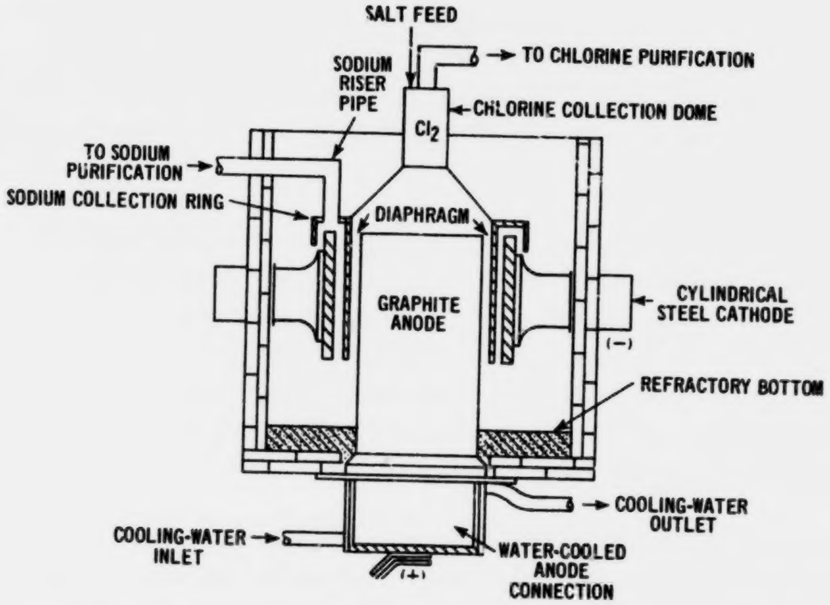
SALT FEED
SODIUM RISER PIPE
TO CHLORINE PURIFICATION
CHLORINE COLLECTION DOME
Cl_2
TO SODIUM PURIFICATION
SODIUM COLLECTION RING
DIAPHRAGM
GRAPHITE ANODE
CYLINDRICAL STEEL CATHODE
(−)
REFRACTORY BOTTOM
COOLING-WATER OUTLET
COOLING-WATER INLET
WATER-COOLED ANODE CONNECTION
(+)

Figure 8. Downs fused-salt electrolytic cell (Source: U.S. Patent 2,913,381).

(1) the use of absorbers or scrubbers employing water, caustic soda, slaked lime, or carbon tetrachloride or (2) the use of blow-gas chloride directly for in-plant processes such as chlorination of organics.

In some sodium-producing plants, including two that responded to the questionnaire used in this study, all the gaseous chlorine is used within the plant for chlorination, a practice that eliminates the liquefaction blow gas and its disposal. Emergency caustic or lime tanks are usually available to absorb gaseous chlorine in case the chlorination process is stopped temporarily and the Downs cells continue to operate.

The Downs cell itself is a source of metal fume emission during startup and diaphragm replacement, which occur at 350- and 20-day intervals, respectively.[14]

The cell startup procedure[15] involves the use of graphite starter blocks, which are wedged between the anode and cathode to serve as current "bridges." After the sodium chloride-calcium chloride mixture is packed around the graphite blocks, current is passed between the electrodes, heating the blocks and melting the surrounding bath. While the electrolyte is melting and the collection dome has not yet been inserted into the electrolyte bath, emissions of calcium and sodium oxides[16] and sodium chloride[17] occur, requiring ventilation hoods directly over the cell to remove the fumes from the cell room. When the bath is sufficiently molten to allow free current flow, the graphite wedges are removed and the collection dome is swung into place. More frequently, the collection dome must be removed to replace the steel diaphragm, although cell shutdown is not required.

The dense white fume formed during cell startup is, in part, sodium oxide that is formed when sodium vapor combines with atmospheric oxygen.

Sittig,[15] writing about the oxidation reaction, reports that "sodium peroxide (Na_2O_2) is probably the initial product which reacts with any excess sodium to give sodium monoxide (Na_2O)." Sodium vapor also combines with chlorine to form white sodium chloride fume during cell startup and diaphragm replacement.

No source sampling of Downs-cell emissions during startup and diaphragm replacement was undertaken for this study and no data on the magnitude of sodium and calcium oxide and sodium chloride emissions are available in the literature. The only reference to the collection of Downs-cell emissions is by McFadyen and Buterbaugh,[16] who state that cell startup fumes may be sent to caustic scrubbers for collection, a practice indicating that the caustic liquor may aid in controlling chlorine emissions.

Sodium oxide fumes may also be emitted during cleaning operations when sodium and salt residues, scraped from cell parts, storage drums, and other equipment, are burned with kerosene. The dense metal oxide fumes from either can be collected by medium-pressure-drop water scrubbers.

Sources of salt emissions during raw material preparation are the primary and secondary salt driers. These can also be controlled by water scrubbers.

MINOR CHEMICAL METHODS

Other methods of chlorine production include the salt process and the electrolysis of hydrochloric acid to form elemental hydrogen and chlorine. These processes are currently operated on a commercial scale in two separate plants in the United States.

Salt Process

Process Description

In the salt process, potassium chloride reacts with nitric acid and oxygen to form potassium nitrate, chlorine gas, and water. The potassium nitrate is a valuable by-product and is dried for use in fertilizers.

The overall reaction is:

$$12KCl + 12HNO_3 + 3O_2 \longleftrightarrow 12KNO_3 + 6Cl_2 + 6H_2O$$

Intermediate steps regenerate nitric acid as illustrated by the following equations:

$$12KCl + 16HNO_3 \longleftrightarrow 12KNO_3 + 4NOCl + 4Cl_2 + 8H_2O \qquad (6)$$

$$4NOCl + 8HNO_3 \longleftrightarrow 12NO_2 + 2Cl_2 + 4H_2O \qquad (7)$$

$$12NO_2 + 6H_2O + 3O_2 \longleftrightarrow 12HNO_3 \qquad (8)$$

Sources and Quantities of Emissions

Emissions of potassium nitrate dust can be expected from drying and prilling operations. The emission of oxide in the absorption process (Equation A),[8] and of acid mist from the handling and storage of nitric acid are also possible.

Electrolysis of Hydrochloric Acid

Process Description

The electrolytic cell is comprised of vertical bipolar graphite electrodes and polyvinyl chloride diaphragms. Hydrochloric acid feed is introduced into the cell at 150° F. The chlorine that comes off at the anode is scrubbed to remove entrained hydrochloric acid and water and dried with sulfuric acid to provide a gaseous chlorine of 99.8 percent purity. The chlorine is then sent to process or liquefaction using the same equipment used in a conventional chlorine plant.

Sources and Quantities of Emissions

Emissions of chlorinated organics and inerts arise from the absorption of process hydrogen chloride in the acid scrubber. The magnitude of those emissions depends upon the yield of the side reactions that occur during chlorination and upon scrubber operating conditions.

CAUSTIC MANUFACTURE BY THE LIME-SODA PROCESS

Some caustic soda was previously produced by the lime-soda process, which consists of reacting soda ash with lime to produce sodium hydroxide and calcium carbonate. This process is of historical significance only, since there were no lime-soda plants known to be operating in the United States at the end of 1969. This situation is primarily the result of the construction of electrolytic chlorine plants that produce caustic as a co-product.

PROCESS DESCRIPTION

The production of sodium hydroxide from soda ash and lime proceeds according to the following reaction:

$$NaCO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3 \qquad (9)$$

Lime for the process is obtained by calcining quarry limestone or the calcium carbonate mud that is produced by the process when lime recycle is practiced. Soda ash is usually supplied by an adjacent plant or from natural deposits of trona ($Na_3H(CO_3)_2 \cdot 2H_2O$). A typical flowsheet for a plant using mud recycle is shown in Figure 9.

To recover lime, it is necessary to wash the precipitated calcium carbonate thoroughly in order to achieve efficient recovery of caustic and unreacted soda ash. Either countercurrent decantation or multistage vacuum filtration has been used to accomplish this.

In countercurrent decantation a series of decanters performs the caustic extraction by washing the carbonate slurry with successively weaker caustic solutions. Water is used for the final wash. The strong caustic stream from the first decanter is sent to a caustic settler to remove traces of solids. The thick carbonate slurry from the last decanter is fed to the reburning kiln for recovery of the lime or it is lagooned and not recycled.

Where vacuum filtering is employed, repulping and washing of the filter cake recover caustic and soda ash from the thick carbonate muds. As in countercurrent washing, caustic-rich filtrates are sent to the caustic settler, while the washed muds are returned to the mud-reburning kiln or lagooned.

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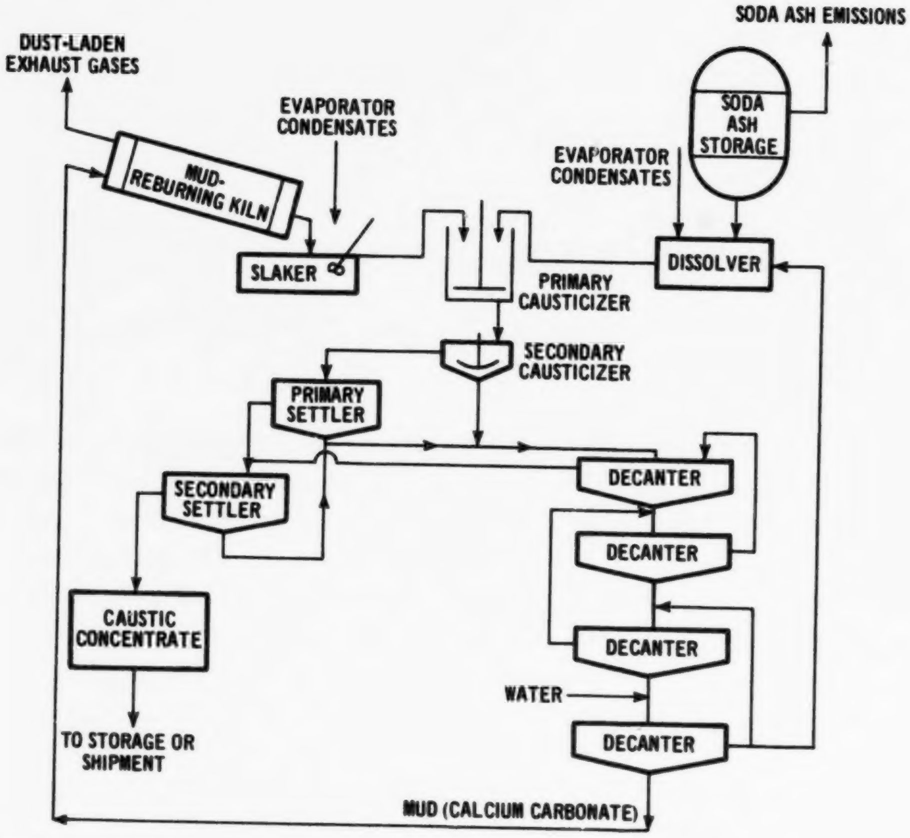
SODA ASH EMISSIONS
DUST-LADEN EXHAUST GASES
EVAPORATOR CONDENSATES
SODA ASH STORAGE
MUD-REBURNING KILN
EVAPORATOR CONDENSATES
SLAKER
PRIMARY CAUSTICIZER
DISSOLVER
SECONDARY CAUSTICIZER
PRIMARY SETTLER
SECONDARY SETTLER
DECANTER
DECANTER
CAUSTIC CONCENTRATE
DECANTER
WATER
TO STORAGE OR SHIPMENT
DECANTER
MUD (CALCIUM CARBONATE)

Figure 9. Flow diagram of lime-soda plant with counter-current decantation.

A rotary kiln is used to roast carbonate mud cake or quarry limestone, producing calcium oxide and carbon dioxide. Mud reburning eliminates the mud disposal problem and produces a relatively pure grade of calcium oxide. Carbon dioxide may be recovered for the manufacture of soda ash in some integrated plants, or it may be vented to the atmosphere.

SOURCES AND QUANTITIES OF EMISSIONS

Emissions from lime-reburning kilns may be controlled by the use of venturi scrubbers. Stuart and Bailey[18] report efficiencies of from 98 to 98.7 percent and losses of 335 to 1,346 pounds per day for a venturi scrubber serving a kiln producing 200 to 292 tons of calcine per day. Collins[19] also performed emission tests on venturi scrubbers controlling kiln emissions and found 0.49 to 0.94 ton per day particulate emissions for a 120-ton-per-day kiln at collection efficiencies of 86 to 97 percent. Collins also found that most of the uncollected particulate was the fine soda fume; thus, thorough washing of the carbonate muds to remove alkali residues will prevent excessive small-particle emissions in lime-reburning kilns. Improved mud washing also prevents excessive ring and ball formation within the kiln.

Kilns also emit carbon dioxide in stoichiometric quantities (0.785 ton of CO_2 per ton of lime, excluding the CO_2 contributed by fuels) if it is not recovered from soda ash manufacture.

Soda ash handling before solution may be a source of particulate emissions from soda lime manufacturing. No figures are available on the quantities or types of control for soda ash emissions. Kayloor[20] reports, however, that soda ash handling (conveyor transfer points, elevators, screens, and storage bins) for a dense soda ash operation created a general housekeeping dust problem that was adequately controlled by a 25,000 cubic feet per minute reverse-jet-type tubular bag collector. Collected soda ash amounted to 6 tons per day.

In another soda ash-handling operation described by Kaylor, dry cyclones and washers collected nearly 2 tons of soda per day, although the reported collection efficiency was only 80 to 90 percent.

Sodium hydroxide fumes, mists, or dusts from the concentration of 50 percent to 73 percent caustic or to fused caustic are the same as those produced by the electrolytic caustic concentration process.

CONTROL OF EMISSIONS

In the chlor-alkali industry, the significant contaminant from the standpoint of emission control is chlorine. Other contaminants include carbon dioxide and carbon monoxide, which are present in cell gas in small quantities, averaging 1 to 2 percent for CO_2 and about 0.02 percent for CO.[9] The following sections deal with the current practices for controlling chlorine emissions in the chlor-alkali industry.

Emissions of chlorine originating from blow gases, tank-car blowdowns, air blowing of mercury-cell brine, and air padding of liquid-chlorine storage tanks can be prevented or controlled by:

1. Using the chlorine so produced for chemical requirements within the plant.
2. Neutralizing the chlorine in alkaline scrubbing units to form disposable, non-volatile substances such as calcium or sodium hypochlorites.
3. Scrubbing the chlorine from the gas streams with a suitable solvent, such as water, alkaline brine, or carbon tetrachloride, with subsequent recovery of the chlorine.

Table 7 summarizes present practices for the treatment of chlorine in blow gas as reported in 24 questionnaire responses.

Table 7. PROCESSING OF BLOW-GAS CHLORINE[a]

Process used	Number of plants
Sent to alkaline scrubbing equipment	7
Sent to absorptive scrubbing equipment	4
Vented to atmosphere	0
Sent to in-plant processes	11
Not indicated	2
Total	24

[a] Data from 24 questionnaire responses

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IN-PLANT USE

Waste chlorine has been used to manufacture chlorobenzene,[21] hydrochloric acid,[22] sulfur monochloride,[23] or bleach.[24] Waste chlorine has also been used to chlorinate river water to prevent algae buildup in cooling towers and to treat waste water before discharge. Eleven of 24 plant questionnaires indicated the use of blow-gas chlorine within the plant.

ALKALINE SCRUBBING SYSTEMS

Alkaline scrubbers, employing caustic or lime to react with the waste chlorine to form salt and hypochlorite, are suited for dilute tail gases (less than 1 percent chlorine). (When chlorine concentrations are higher – in the range of several percent – other control methods permitting recovery of pure chlorine are more attractive economically.) Absorption efficiences of nearly 100 percent (Appendix A) are attainable at modest equipment costs. Operating costs can be minimized if the plant produces excess caustic liquor, because the liquor can be used for scrubbing. Waste chlorine in the blow gas from the liquefaction system and that originating from the air blowing of depleted brine and other sources are generally combined and sent to a countercurrent packed tower using caustic liquor or a spray tower using a lime slurry. As the blow gas proceeds through the scrubbing system, one of the following reactions takes place as chlorine is removed from the waste-gas stream:

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O \tag{10}$$

$$2Ca(OH)_2 + 2Cl_2 \longleftrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O \tag{11}$$

Both reactions are exothermic, proceed rapidly to completion, and are irreversible over a wide range of concentrations, if high temperatures and low pH are avoided.[25] Any carbon dioxide in the gas stream will consume alkali. The consumption of alkali can be reduced by controlling the temperature and pH so that some bicarbonate is formed.

Packed towers usually employ Raschig rings or ceramic packings to increase contact with the waste chlorine and caustic. Milk-of-lime scrubbers use sprays, cascade baffles, or falling films to avoid clogging and disintegration of the packing.

The chlorine content of waste gases sent to the alkaline scrubbers varies from 0.1 to 30 percent (Appendix A, Tables A-1 and A-2), depending upon the sources of waste chlorine and the amount of dilution air present.

Air blowing of depleted brine produces chlorine concentrations of about 500 ppm whereas concentrations in vent gases from liquefaction systems are usually greater than 10 percent by volume.

Seven of the 24 plants responding to the questionnaires use alkaline scrubbers to control blow-gas emissions. Three of these plants use lime slurry as the scrubbing agent, three use caustic solution, and one uses a mixture of caustic, sodium carbonate, and sodium bicarbonate. One of the plants using lime employs vats for scrubbing waste chlorine. Absorption efficiencies exceeding 99 percent were given for all plants. Source tests were performed on two lime scrubbers and one caustic scrubber. Absorption efficiencies of 99.9 percent or higher and exit chlorine concentrations of less than 10 ppm in the vents were found in all three cases.

ABSORBERS

In contrast to scrubbing systems involving neutralization and disposal of chlorine, various absorption techniques can be used to recover waste chlorine. This is especially useful where high chlorine concentrations (greater than 10 percent) favor economic recovery of chlorine. Such systems contain an absorber to remove chlorine from the gas stream and a stripper to recover the absorbed chlorine from the rich absorbing liquor. Collection efficiencies will generally be better than 90 percent.

Water

Blow-gas columns using water for absorption (Figure 10) are particularly useful in some diaphragm-cell chlorine plants. A cooler-stripper is integrated into the main cell chlorine purification system. Cold water is passed countercurrent to the chlorine-containing gas stream in an absorption tower filled with ceramic packing. Overhead gases, too low in chlorine for its economical recovery, can be sent to alkaline scrubbers or discharged to the atmosphere. Bottoms from the tower, rich in dissolved chlorine, are sent to a desorption tower consisting of a direct-contact cooler and a steam-stripping section. Hot chlorine cell gas is used to strip the chlorine partially from the cold water while the cell gas is simultaneously cooled. The remaining chlorine is removed by direct contact with live steam. Two plants responding to the questionnaire indicated that water absorbers are used to control blow-gas emissions. One of these, having exit chlorine concentrations of 3 percent, directs vent gases to a caustic scrubber that virtually eliminates chlorine emissions to the atmosphere. The other plant uses an absorber designed to give an absorption efficiency of 97 percent, corresponding to an exit chlorine concentration of 0.3 percent. Normally a blow-gas water absorber is operated at 95 to 97 percent absorption efficiency and the unabsorbed chlorine is vented to the atmosphere. If such vent gases are considered to contain chlorine in excess of allowable limits, absorption efficiencies as high as 99.4 percent can be obtained at a somewhat higher cost, the cost of the steam used in stripping. As an alternative, a secondary water scrubber can be used, with the water effluent sent to the sewer. In any event, it is good practice to provide an alkaline scrubber for emergency use in case the chlorine in the vent gases should become excessive.

Stack tests performed in one plant for this study found chlorine absorption efficiencies ranging from 72.5 to 99.4 percent. The efficiency of 72.5 percent, which is unusually low, was obtained when the scrubber was operating under foaming conditions caused by the experimental use of amines for treating the

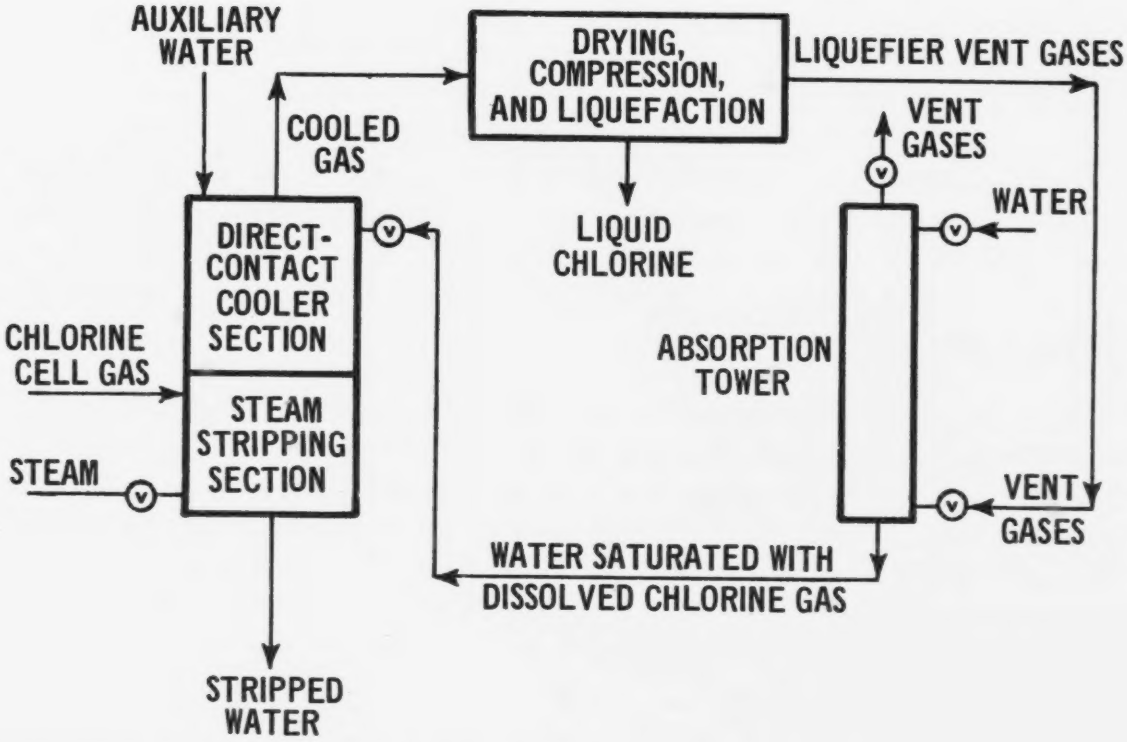
AUXILIARY WATER
COOLED GAS
DRYING, COMPRESSION, AND LIQUEFACTION
LIQUEFIER VENT GASES
VENT GASES
WATER
LIQUID CHLORINE
DIRECT-CONTACT COOLER SECTION
CHLORINE CELL GAS
STEAM STRIPPING SECTION
STEAM
ABSORPTION TOWER
VENT GASES
WATER SATURATED WITH DISSOLVED CHLORINE GAS
STRIPPED WATER

Figure 10. Recovery of blow-gas chlorine by water absorption (Source: U.S. Patent 2,750,002).

scrubber water. Mass chlorine efficiencies are dependent upon gas-to-liquid ratios, the effects of which are shown in Table 8.

Table 8. EFFECT OF LIQUID-GAS RATIO UPON CHLORINE ABSORPTION EFFICIENCY[a]

Inlet gas flow, scfm[b]	Water flow, gal/ min	L/G ratio, gal/scfm	Mass chlorine efficiency, %
191	115	0.60	72.5[c]
184	112	0.61	91.0
163	112	0.69	97.4
139	112	0.81	99.4

[a] These data, from Plant 30, are used in Appendix E to calculate the economical optimum operation of a blow-gas water absorber.

[b] At 32°F, 1 atm, wet.

[c] Foaming in scrubber caused by experimental amine treatment of cooling water. At the liquid-gas (L/G) ratio used, the expected efficiency would be in the range of 90 percent.

Carbon Tetrachloride[26]

Another type of blow-gas absorber uses carbon tetrachloride as the solvent to recover chlorine from gas streams. Carbon tetrachloride contacts the waste chlorine in a packed tower and releases it in a steam-heated stripper.

The chlorine-containing gas stream is compressed and cooled to condense part of the chlorine before it is fed to the absorber. The chlorine-rich carbon tetrachloride solution is stripped of chlorine in a recovery tower consisting of a stripping section and a rectifying section (Figure 11).

Literature references and one questionnaire indicate that chlorine recovery in the absorber is essentially 100 percent. No stack tests were made, however, in plants using carbon tetrachloride absorbers.

Sulfur Monochloride

A third and less common absorption system uses sulfur monochloride to recover waste chlorine according to the following reaction:

$$Cl_2 + S_2Cl_2 \longleftrightarrow 2SCl_2 \qquad (12)$$

Sulfur monochloride contacts chlorine-rich blow gas in an absorber, forming sulfur dichloride. Chlorine is then distilled from the dichloride and is recovered while the resulting monochloride is recycled to the absorption tower. A variation of the process reacts chlorine with sulfur monochloride. The resulting mixture of mono- and dichlorides is marketed by some plants. The process is unpatented, however, and is not reported in the literature.

Other Absorption Systems

Other patented systems include those using alkaline brine,[26] stannic chloride,[27] hexachlorobutadiene,[28] and ethylene dichloride.[29] The alkaline brine system is used in mercury-cell plants to some extent; however, the other three systems have no commercial significance.

ADSORPTION SYSTEMS

A patented recovery system uses silica gel to adsorb chlorine from waste streams.[30] Recovery efficiencies of 90 to 98 percent are claimed. Chlorine can also be removed from very dilute gas streams by means of activated carbon. The carbon can be reactivated by hydrogen gas at nominal pressures and temperatures, forming hydrochloric acid, which can be readily absorbed in water.[3]

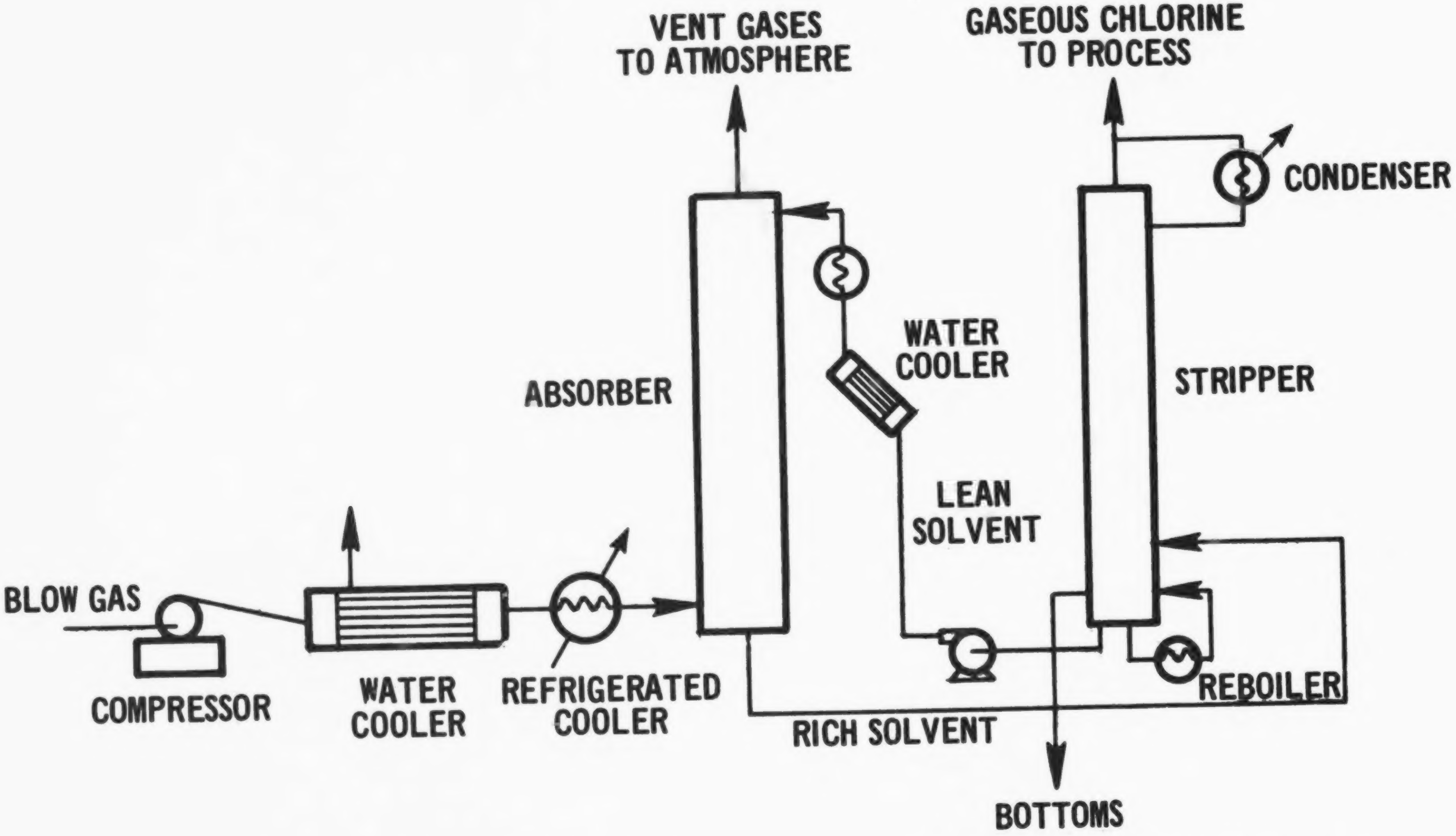
VENT GASES
TO ATMOSPHERE
GASEOUS CHLORINE
TO PROCESS
CONDENSER
ABSORBER
WATER
COOLER
STRIPPER
LEAN
SOLVENT
BLOW GAS
COMPRESSOR
WATER
COOLER
REFRIGERATED
COOLER
RICH SOLVENT
REBOILER
BOTTOMS

Figure 11. Recovery of blow-gas chlorine by carbon tetrachloride absorption (Source: U.S. Patent 2,765,873).

GLOSSARY OF TERMS

ABBREVIATIONS

abs	Absolute
amps	Amperes
atm	Atmosphere
°Be	Degrees Baumé $\text{Sp. gr.} = \frac{145}{145-°\text{Be}}$
Btu	British thermal units
cal	Calories
cc	Cubic centimeter
cfm	Cubic feet per minute
°C	Degrees centigrade
ft^3	Cubic feet
°F	Degrees Fahrenheit
gal	Gallons
gal/min	Gallons per minute
g	Grams
gr	Grains (1 grain = 64.8 milligrams)
ID	Inside diameter
in. H_2O	Inches of water
in. Hg	Inches of mercury
kcal	Kilocalorie
l.	Liter
lb	Pounds
L/G	Liquid to gas ratio in mass units
m	Meters
mg	Milligram
ml	Milliliter
mm	Millimeter
mol	Mole
N	Normal
OD	Outside diameter
ppm	Parts per million
psia	Pounds per square inch absolute
psig	Pounds per square inch gauge
scf	Standard cubic feet measured at 0° C (32° F) and 760 mm (29.92 in.) Hg
scfm	Standard cubic feet per minute
sec	Second
sp. gr.	Specific gravity
V	Volts

CHEMICAL SYMBOLS

$AgCl$	Silver chloride
$AgNO_3$	Silver nitrate
Ba	Barium
$BaCl_2$	Barium chloride
$BaCO_3$	Barium carbonate
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
Cl_2	Chlorine
CO	Carbon monoxide
CO_2	Carbon dioxide
CCl_4	Carbon tetrachloride
Cr	Chromium
Fe	Iron
$FeCl_3$	Ferric chloride
H_2	Hydrogen
H_2O	Water
HCl	Hydrogen chloride
Hg	Mercury
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
KCl	Potassium chloride
KOH	Potassium hydroxide
Mg	Magnesium
$MgCl_2$	Magnesium chloride
Mo	Molybdenum
N_2	Nitrogen
Na	Sodium
Na_2O	Sodium monoxide
Na_2O_2	Sodium peroxide
$NaCl$	Sodium chloride
Na_2CO_3	Sodium carbonate
$NaSO_4$	Sodium sulfate
NH_4CNS	Ammonium thiocyanate
O_2	Oxygen
SCl_2	Sulfur dichloride
S_2Cl_2	Sulfur monochloride
Ti	Titanium
V	Vanadium

DEFINITIONS

Absorber	Within the context of this report, a tower in which a falling liquid absorbs a gas, such as a blow-gas absorber that preferentially removes chlorine from a chlorine-air mixture. It may be packed, spray, or bubble cap in design.
Air blowing	Passing air upward through a liquid to remove dissolved gases.
Air padding	Use of compressed air above the surface of a liquid to transfer the liquid to another vessel.
Amalgam	An alloy of mercury with another metal such as sodium or potassium.
Anode	The positive pole of an electrolytic cell.
Blow gas	Chlorine-inert gas mixture separated from liquid chlorine; also known as sniff gas or tail gas.
Cathode	The negative pole of an electrolytic cell.
Cell gas	Chlorine gas from an electrolytic cell.
Contact cooler	A tower in which a liquid is used to cool a gas by direct contact.
Diaphragm	A porous asbestos coating over the cathode screen of a diaphragm-type cell that separates the chlorine gas evolved at the anode from the hydrogen gas evolved at the cathode.
Denuder	The section of mercury-cathode cell where the sodium or potassium amalgam is reacted with water to form caustic and hydrogen.
Effluent	Exit gas or liquid stream containing pollutants.
Electrolyzer	The section of a mercury-cathode cell where electrolytic decomposition of brine takes place.
Emission	Any gas stream emitted to the atmosphere.
Establishment	A plant or manufacturing unit.
Explosion disc	See frangible disc.
Frangible disc	A disc, installed between pipe flanges, designed to fail at a predetermined pressure.
"Gunk"	Liquid or solid impurities, or both, present in gaseous or liquid chlorine.

Header	A pipe into which several other pipes are connected.
Heel	Residual liquid left in a vessel after a portion of its contents has been discharged.
Padding	See air padding.
Safety valve	A valve designed to open at a predetermined pressure.
Safety disc	See frangible disc.
Stripper	Within the context of this report, a tower in which chlorine-rich solvent is heated to recover chlorine as gas.

APPENDICES

A. EMISSIONS FROM CHLOR-ALKALI PLANTS

B. SAMPLING AND ANALYTICAL TECHNIQUES

C. PHYSICAL DATA

D. CHLORINE-CAUSTIC, FUSED-SALT, AND LIME-SODA ESTABLISHMENTS IN UNITED STATES, JANUARY 1970

E. FIELD TEST OF ABSORPTION EFFICIENCY OF BLOW-GAS ABSORBER

APPENDIX A: EMISSIONS FROM CHLOR-ALKALI PLANTS

Most of the emission and operating data (Table A-1) in Appendix A were supplied by the manufacturers of chlorine and caustic. The emission data represent results obtained from questionnaires sent to 39 chlorine establishments and from stack-sampling programs conducted jointly by the Manufacturing Chemists' Association and the Public Health Service (Tables A-2 and A-3).

Following the emission and operating data are a field test of potential chlorine emissions using air for liquid chlorine transfer (Table A-4, Figure A-1), and the calculated potential chlorine emissions from blow gas.

FIELD TEST OF POTENTIAL CHLORINE EMISSIONS, USING AIR FOR LIQUID CHLORINE TRANSFER

The test data in Table A-4 (also shown in Figure A-1), supplied by Hooker Chemical Corporation, relate the increase in chlorine in the vent gas of a "padded" liquid chlorine tank as the pressure in the tanks is released and that present after the liquid chlorine has been transferred. The tank was air padded at 125 pounds gauge for 4 hours prior to the transfer, which required an additional 5.25 hours. A 5-ton "heel" of residual chlorine was present in the tank during the venting period.

CALCULATED POTENTIAL CHLORINE EMISSIONS FROM BLOW GAS

As stated in the chapter on diaphragm and mercury cells, the principal emission from chlorine manufacture is the chlorine present in the so-called inerts that are separated from the liquid chlorine during liquefaction.

This gaseous mixture, along with blow gas, may be returned or recycled to the chlorine system for chlorine recovery; it may be absorbed in water or other absorbants for chlorine recovery or manufacture of useful by-products, or both; or it may be neutralized to minimize or prevent emissions to the atmosphere. Under some circumstances the blow gas may be vented, in which case the potential emissions become actual emissions. Even with chlorine recovery or neutralizing systems, the efficiency is less than 100 percent and some chlorine is emitted to the atmosphere.

The amount of chlorine in the blow gas is a function of operating conditions and can be calculated from the partial pressure of chlorine in the blow gas. A fraction of a percent of hydrogen is present in the inert gases. In some cases the

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Table A-1. EMISSION AND OPERATING DATA FROM CHLOR-ALKALI ESTABLISHMENTS USING BLOW-GAS TREATMENT[a]

	Plant number						
	28	29	30				31
Chlorine production, tons/day	490	140	180[b]	170[c]	149[c]	119[c]	316
Liquid chlorine capacity, tons/day	370	140	180[b]	170[c]	149[c]	119[c]	316
Cell type[d]	M and D	M	D				M
Description of control equipment	Two milk-of-lime falling film towers	Two caustic-packed towers in parallel	Packed-tower water absorbed under pressure				Two milk-of-lime cascade baffle towers in parallel
Tower diameter, in. OD	56	52[e]	42				60
Height of packing, ft	30.5[f]	6.83	29				12[f]
Type of packing	None; 4-in. standard pipe launderer	2-in. Intalox saddles and ceramic tiles	Alternately stacked 1- and 1-1/2 in. Intalox saddles				None; 3-ft overlapping baffles
Materials of tower construction	Concrete sections	Titanium-lined steel	Rubber-lined steel				Hetron, glass-matte reinforced
Sources of inlet chlorine	Blow gas, process blowdown, tank car venting	Blow gas, brine blowing, process blowdown, tank car venting	Blow gas only				Blow gas,[g] cell end boxes, tank car vents
Scrubbing liquor and strength at test, % by wt	$Ca(OH)_2$ 17	NaOH 4 and 17	H_2O				$Ca(OH)_2$ 3.2
Liquor circulation rate, gal/min	550	75	115	112	112	112	200
Liquor temperature, °F	N.M.[h]	N.M.	52	75	75	75	109
Scrubber pressure drop, in. H_2O	2.5	2	3	4	4	3.5	2
Scrubber							
Inlet gas rate, scfm at 32° F, 1 atm wet	N.M.	N.M.	191	184	163	139	N.M.
Outlet gas rate, scfm at 32° F, 1 atm wet	456	4,140[i]	171[j]	151[j]	127[j]	106[j]	1,120[i]
Inlet chlorine concentration, vol %, wet	19.7	0.325	14.4	14.1	13.9	13.1	1.41
Outlet chlorine concentration, vol %, wet	0.0009	N.D.[k]	4.46[l]	1.55	0.44	0.1	0.0008
Inlet carbon dioxide concn., vol %, wet	N.M.	N.M.	18.0	22.4	22.4	22.3	N.D.
Outlet carbon dioxide concn., vol %, wet	N.M.	N.M.	19.6	21.6	18.6	15.2[m]	N.D.
Chlorine mass efficiency, %	99.9	>99.9	72.5[l]	91.0	97.4	99.4	>99.9
Chlorine emitted, lb/day	1.16	None	2,130	659	158	29.6	0.284
Chlorine emission factor, lb chlorine/100 tons chlorine liquefied	0.314	None	1.090	388	106	24.9	0.095
Stack plume opacity, %	80	40	N.O.[o]	N.O.	N.O.	N.O.	—[n]

[a] Based on sampling by the Public Health Service.

[b] Actual liquid production at time of test was 195 tons/day. Production changed to 180 tons/day to agree with total chlorine in blow gas/100 tons chlorine liquefied for tests 2, 3, and 4 performed at a later date.

[c] Liquid production based upon absorber chlorine load.

[d] D = diaphragm; M = mercury.

[e] Inside diameter.

[f] Height of towers, no packing employed.

[g] After scrubbing in alkaline brine.

[h] Not measured.

[i] Combined exhaust rate from both stacks.

[j] Calculated by material balance.

[k] Not detected.

[l] Foaming present in scrubber.

[m] Determined by extrapolation.

[n] Exhaust sent to powerhouse stack.

[o] No observation.

Table A-2. QUESTIONNAIRE EMISSION DATA FROM CHLOR-ALKALI PLANTS WITH BLOW-GAS TREATMENT EQUIPMENT

	Plant number										
	1	4	7	9	10	12	13	14	18	22	25[a]
Type of cell	D[b]	D	D	D	M	M	M	M	M	M	D
Rated capacity, tons/day	240	50[c]	65	50	230	260	130	112	262	180[c]	458[d]
Scrubbing liquor	5% NaOH	5% NaOH	H_2O	$Ca(OH)_2$[e]	$Ca(OH)_2$	$Ca(OH)_2$	Na(OH)	Waste alkali[f]	CCl_4	–	H_2O
Liquor flow, gal/min	25	10	80	N.A.[g]	2	600	73	50	17	–	550
Inlet liquor conditions											
Nominal Cl Concn., g/liter	60	1	0	N.A.	0	10	0	0	0.01[h]	–	0
Temperature, °C	21	20	20	N.A.	30	30	28	30	-18	–	32.2
Outlet liquor conditions											
Nominal Cl concn., g/liter	120	2	?	N.A.	150	20	33	?	9.4[h]	–	1.23
Temperature, °C	21	22	20	N.A.	30	32	40	35	10	–	32.2
Tower diameter, in.	30	10	24	N.A.	72	72	72	72	42[f] 29[i]	38	48
Height of packing, ft	17	20	30	N.A.	32	32	20	40	50[j] 50[i]	20	20
Type of packing	2-in. Raschig rings	1-in. Raschig rings	1.5-in. Intalox saddles	N.A.	Spray tower	Raschig rings	Chemical stoneware rings	8 × 12-in. clay tile	Plates[j] 1-in. Raschig[i]	3-in. ceramic partition rings	2-in. ceramic Berl saddles
Materials of construction	Rubber-lined steel	Rubber-lined steel	Rubber-lined steel	N.A.	Concrete	Concrete	Concrete	Concrete	Steel	Rubber-lined steel	Rubber-lined steel
Inlet gas temp., °C	4	-60	25	35	20	40	3	35 to 40	100	-10	-38
pressure, psig	2	0.1	35	35	0.5	0.14	15	35	95	5	35
chlorine, vol. %	2	0.1	26	7	9	1	15	7	30	5.2	11
Outlet gas temp., °C	21	-10	20	–	25	32	40	30 to 35	30	20	32.2
pressure, psig	0	0	34.66	0	0	0	0	0	40	0	35.0
chlorine, vol. %	0	0	3	0	0	0	0	N.D.[k]	0	0.5	0.3[a]
Outlet gas flow, scfm	1,078	8	14.5	180	390	600	120	370	–	510	202
Efficiency of scrubber, %	100	>99	1	>99	100	100	100	>99	100	90	97
Total chlorine emitted, tons/day	nil	<0.1	0	N.A.	N.D.	N.D.	N.D.	N.D.	nil	0.4	0.084
Lb chlorine emitted solidus 100 tons of liquid chlorine	–	<400	–	–	–	–	–	–	–	<400	54

[a] Design data.

[b] D = diaphragm; M = mercury.

[c] All output is liquid Cl_2.

[d] Liquid Cl_2 product = 308 tons/day.

[e] Reported use of vats containing $Ca(OH)_2$ slurry.

[f] NaOH, $NaHCO_3$, Na_2CO_3.

[g] Not applicable.

[h] Mole %.

[i] Stripper.

[j] Absorber.

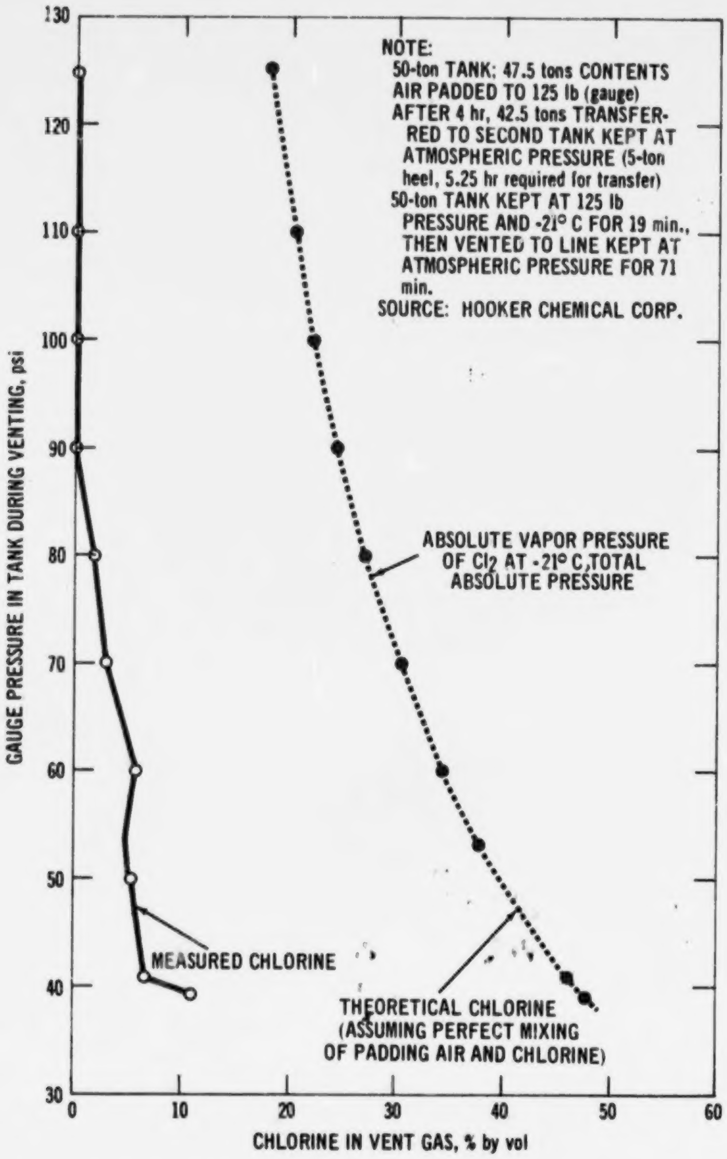
[k] Not detectable by odor.

[l] Water absorber vented to caustic scrubber; chlorine emissions reported as zero.

Table A-3. QUESTIONNAIRE DATA ON HANDLING OF CHLORINE FROM SHIPPING-CONTAINER VENTS DURING LOADING

	Plant number																		
	1	2	3	4	6	7	8	9	10	11	12	13	14	15	19	20	21	22	25
Rated capacity, tons/day	240	180	150	50	70	65	180	50	230	79	260	130	112	254	222	138	190	180	458
Liquid capacity, tons/day Cl_2	240	a	a	50	a	69	a	a	230	a	250	100	112	a	a	a	a	100	308
Quantities of Cl_2, from tank car loading, tons/day	2	0.1	0.1	0.2	<0.1	<1.0	2.0	0.25 to 0.50	0.2	1 to 2	1	3.0	2.0	1.0	1.0	1.0	243	0.3	5.6
Frequency of tank car loading, no./day	3	2[b]	1	1	c	a	a	1	d	e	1	e	f	2	1	d	g	25	g
Tons of chlorine evolved/55-ton tank car loading	0.67	0.35	0.1	0.2	–	–	–	0.25 to 0.50	–	–	1.0	–	–	0.5	1.0	–	–	0.01	–
Tons of chlorine evolved/100 tons of chlorine liquefied	0.84	0.055	0.067	0.4	<0.14	<1.45	1.1	0.5 to 1.0	0.087	1.3 to 2.5	0.40	3.0	1.8	0.39	0.45	0.72	1.28	0.167	1.22
Treatment of tank car waste chlorine:																			
Scrubber	x	–	x	x	x	–	–	x	x	–	x	x	x	–	x	–	–	x	x
In-plant	–	x	–	–	–	x	x	x	–	x	–	–	–	x	x	x	x	–	–
Vent	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	h	i	–	–

[a] Unknown.
[b] Per week.
[c] Rare.
[d] Intermittent.
[e] 8-hr day.
[f] 6-hr day
[g] Daily.
[h] 0.5 % vented = 10 lb/day.
[i] 140 lb/day vented.



NOTE:
50-ton TANK; 47.5 tons CONTENTS AIR PADDED TO 125 lb (gauge)
AFTER 4 hr, 42.5 tons TRANSFERRED TO SECOND TANK KEPT AT ATMOSPHERIC PRESSURE (5-ton heel, 5.25 hr required for transfer)
50-ton TANK KEPT AT 125 lb PRESSURE AND -21° C FOR 19 min., THEN VENTED TO LINE KEPT AT ATMOSPHERIC PRESSURE FOR 71 min.
SOURCE: HOOKER CHEMICAL CORP.

Figure A-1. Chlorine in vent gas from air-padded liquid chlorine tank.

hydrogen content may be sufficiently large to form an explosive mixture in or at the exit of the chlorine liquefier. To prevent this, it is common practice to admit dry air to the chlorine system prior to the condenser. Any additional air at this point acts as inerts and increases the potential chlorine emissions. Calculations of the chlorine present in the blow gas from both diaphragm and mercury cells can be explained best by an example.

Let us assume the following plant operating conditions:

Main chlorine gas from cells (after drying and compressing):

95% chlorine by volume
0.5% hydrogen by volume (0.2 to 0.3% normal range)
4.5% inerts by volume (other than H_2)

Table A-4. CHLORINE IN AIR VENTS FROM TRANSFER OF LIQUID CHLORINE IN STORAGE

Tank pressure, psig	Chlorine in vent gas, vol %
125	Trace[a]
110	Trace[a]
100	Trace[a]
90	Trace[a]
80	2.0
70	3.0
60	5.75
53	5.0
41	6.25
39	11.0

[a] Air padding intake and sampling nozzle at top of tank, along with the greater density of chlorine gas with respect to air, result in comparatively little mixing of the padding air with the chlorine gas above the liquid contents. To calculate the pounds of chlorine lost in each incremental pressure drop, the following expression was employed:

$$\left[\text{lb/day } Cl_2\right]_{\Delta P} + \frac{\left(CV_T \cdot \Delta P\right)\ 71}{RT} \qquad \text{(A-1)}$$

Where: C = concentration of chlorine over the pressure interval, vol %

V_T = volume of the tank, 1,155 ft^3

P = increment at pressure, psi

T = temperature of chlorine, -21°C

$$R = 19.3\ \frac{(\text{psi})\ (\text{ft}^3)}{(\text{1b mole})\ (^\circ\text{K})}$$

The total chlorine emitted during the venting is obtained by adding all the increments.

Such a calculation for the data given in Table A-4 reveals that a total of 33.7 pounds of chlorine is released in transferring 42.5 tons of liquid chlorine. If three transfers of chlorine are assumed, then

$$\frac{3 \times 33.7}{2{,}000} \times \frac{100}{42.5} = 0.119 \text{ ton/100 tons of liquid}$$

chlorine would be vented to the caustic scrubber, or to the atmosphere, as the case may be.

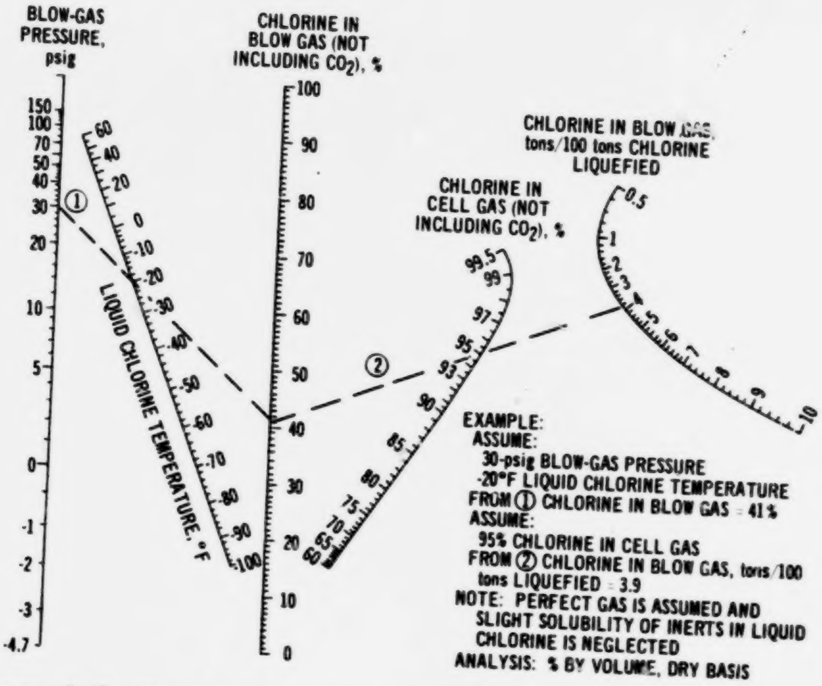
Blow gas (at purge trap):

30 psig
-11° F (same temperature as liquid chlorine)
No recycle of chlorine to the main chlorine system.

From the vapor pressure curve for chlorine (Figure C-4, Appendix C) the vapor pressure of liquid chlorine at -11° F equals 7.65 psig. Thus the percentage of chlorine in the blow gas, on the assumption that there is no air dilution to lower the hydrogen percentage in the vent, is

$$\frac{(\ 7.65 + 14.7)\ \text{absolute vapor pressure}}{(30 + 14.7)\ \text{absolute total pressure}} = 50\%$$

This relationship of percentage of chlorine in blow gas versus liquid chlorine temperature and pressure is shown in the nomograph, Figure A-2. In addition, if the percentage chlorine in the main gas and that in the blow gas are known, one can compute the potential loss of chlorine in the blow gas as tons per 100 tons of chlorine liquefied. For example, let us assume that the blow gas goes to an absorber where all the chlorine is absorbed to make a useful by-product or to be neutralized and wasted. As chlorine is condensed, the inerts in the main gas, originally 5 percent by volume, will remain unliquefied and will be concentrated in the blow gas to 50 percent by volume. Since the chlorine in the blow gas is also 50 percent by volume, the weight ratio of chlorine will be 5/95 (100), or 5.26 tons per 100 tons of chlorine as cell gas. We have assumed that the chlorine in the blow gas is not recycled back into the chlorine system; therefore, the chlorine in the blow gas equals 5.26/(100-5.26), or 5.55 tons per



EXAMPLE:
ASSUME:
30-psig BLOW-GAS PRESSURE
-20°F LIQUID CHLORINE TEMPERATURE
FROM ① CHLORINE IN BLOW GAS = 41%
ASSUME:
95% CHLORINE IN CELL GAS
FROM ② CHLORINE IN BLOW GAS, tons/100 tons LIQUEFIED = 3.9
NOTE: PERFECT GAS IS ASSUMED AND SLIGHT SOLUBILITY OF INERTS IN LIQUID CHLORINE IS NEGLECTED
ANALYSIS: % BY VOLUME, DRY BASIS

Figure A-2. Nomograph for determining chlorine in blow gas with no air dilution and no recycle of chlorine in blow gas.

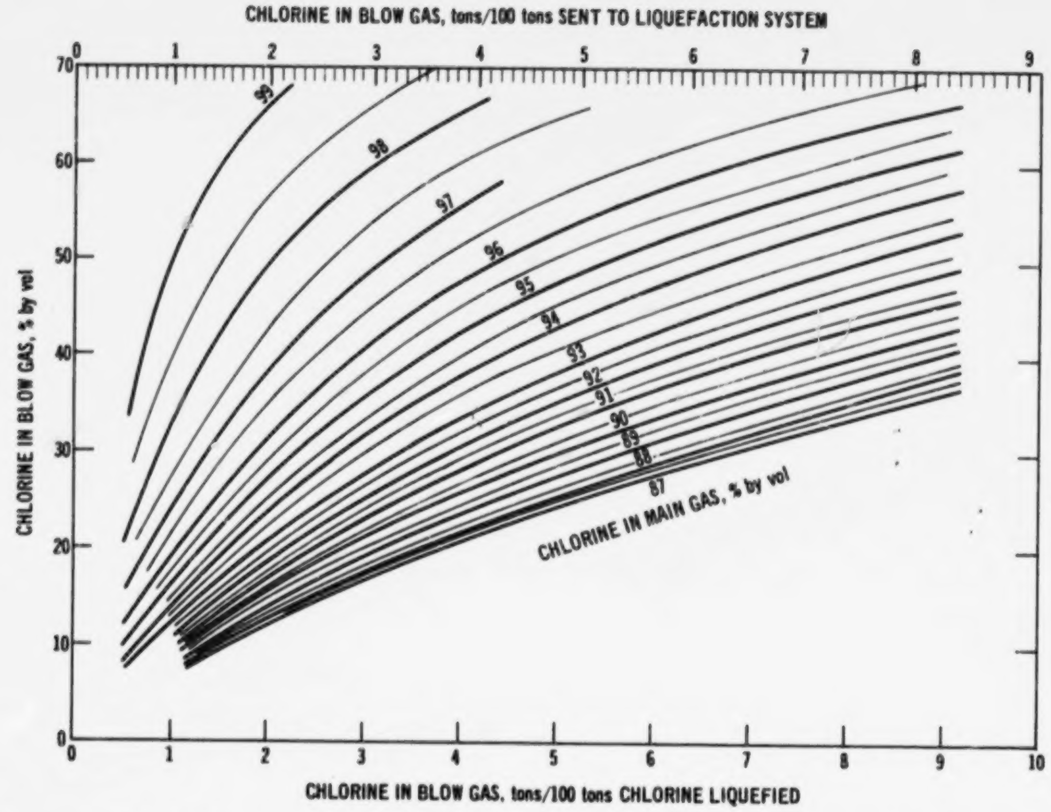


Figure A-3. Chlorine in blow gas versus chlorine in main gas and blow gas with no dilution air and no recycle of chlorine in blow gas.

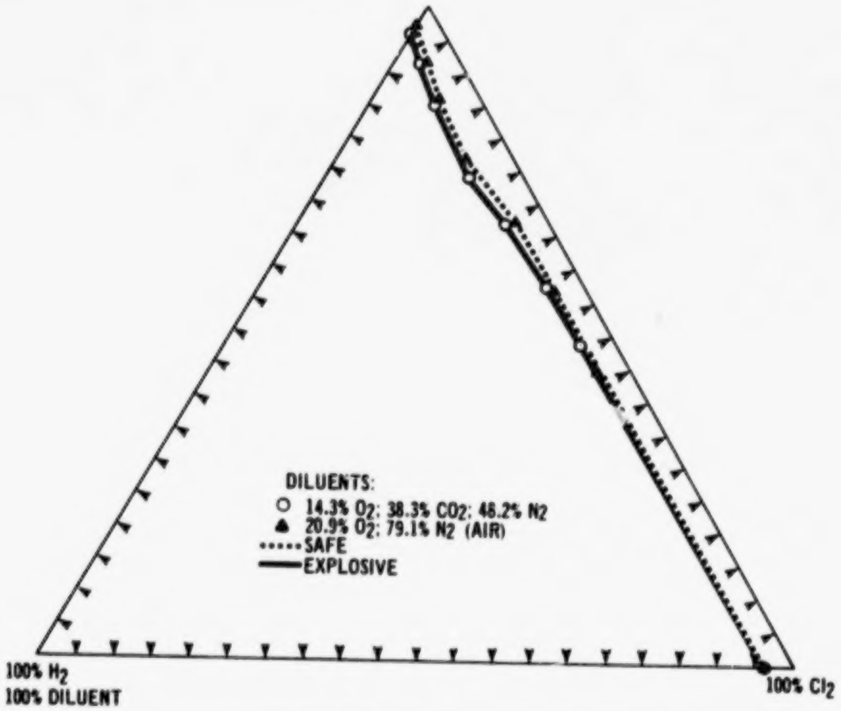
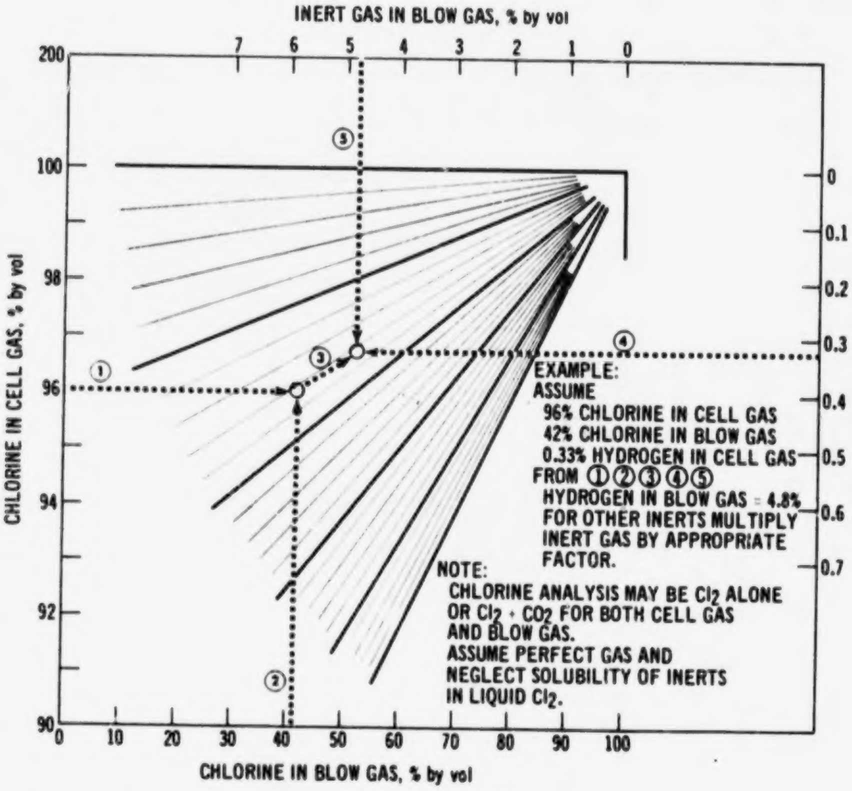


Figure A-4. Lower explosive limits for hydrogen-chlorine mixtures at 3.0 atmospheres (absolute).

100 tons liquefied. This relationship, shown in Figures A-2 and A-3, represents the chlorine used to make a by-product or the loss of product if the chlorine in the blow gas is neutralized or vented to the atmosphere. It also represents the actual emissions to the atmosphere in the event that a blow-gas absorber is not used or becomes inoperative. Figure A-4 indicates the lower explosive limit of hydrogen in the presence of chlorine and in the normal composition of cell gas inerts. A safe upper limit of hydrogen in cell gas inerts is about 5 percent. In the example above, the inerts in the cell gas were 5 percent by volume, which included 0.5 percent hydrogen. The inerts entering the blow-gas absorber will therefore contain 50/5 (0.5) or 5 percent hydrogen.

The relationship of chlorine in cell gas and blow gas to inerts in cell gas and blow gas is shown in Figure A-5. In the preceding example, 50 percent of the blow gas was chlorine. Since the hydrogen content at the entrance to the blow-gas absorber is 5 percent, the hydrogen content of the exit gas after scrubbing out the chlorine will be 2 times 5, or 10 percent. The relationship of chlorine and hydrogen in the main gas to hydrogen at the exit from the blow-gas absorber is shown in Figure A-6.

In the preceding example, note that 10 percent hydrogen in the blow-gas absorber vent is above the lower explosive limit. If the inerts are doubled by adding dilution air at or before the exit of the blow-gas absorber, the hydrogen at the absorber vent will be reduced from 10 to 5 percent, which is considered a safe limit. The inerts in the main gas were 5 cubic feet per 95 cubic feet of



EXAMPLE:
ASSUME
96% CHLORINE IN CELL GAS
42% CHLORINE IN BLOW GAS
0.33% HYDROGEN IN CELL GAS
FROM ①②③④⑤
HYDROGEN IN BLOW GAS = 4.8%
FOR OTHER INERTS MULTIPLY INERT GAS BY APPROPRIATE FACTOR.

NOTE:
CHLORINE ANALYSIS MAY BE Cl_2 ALONE OR $Cl_2 + CO_2$ FOR BOTH CELL GAS AND BLOW GAS.
ASSUME PERFECT GAS AND NEGLECT SOLUBILITY OF INERTS IN LIQUID Cl_2.

Figure A-5. Relationship of chlorine and inerts in cell gas and blow gas (with no air dilution).

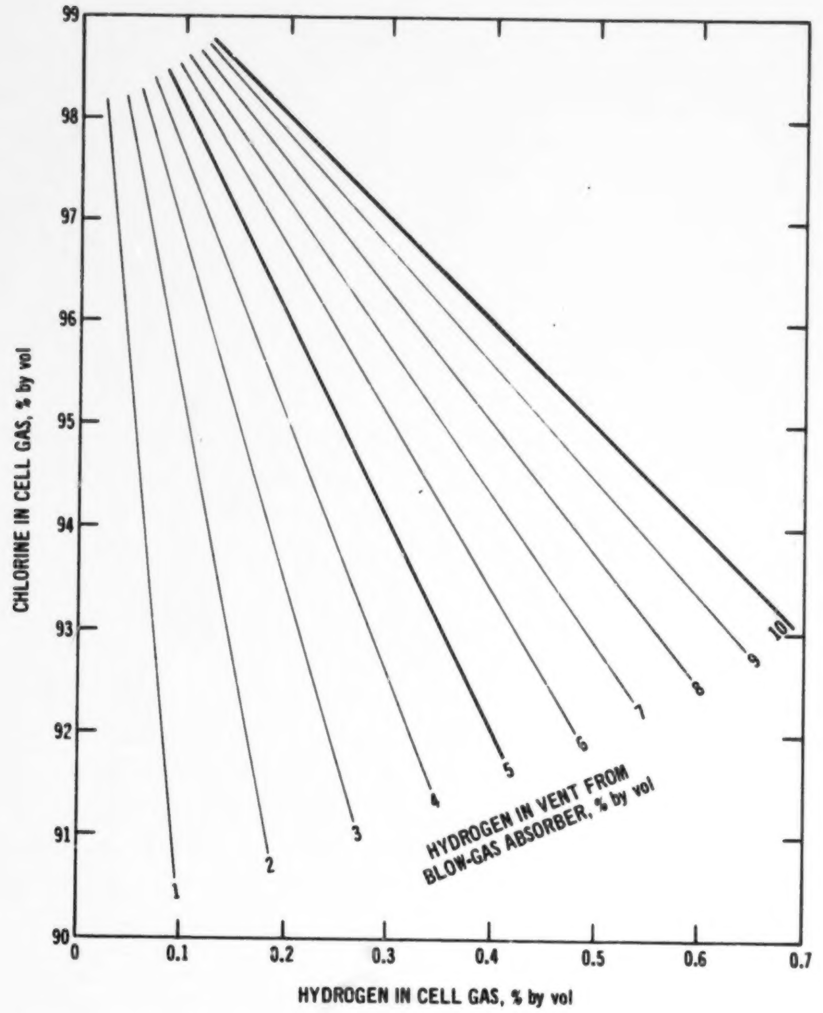


Figure A-6. Hydrogen in vent from blow-gas absorber (with no air dilution).

chlorine. By doubling the inerts, an additional 5 cubic feet of air is added to the chlorine system. Cell gas at a rate of 100 tons per day represents (100)(2000)(5.06)/1440 = 703 scfm. The dilution air required is thus 5/95 times 703, or 37 scfm per 100 tons per day of chlorine as cell gas. The dilution air required for various percentages of chlorine and hydrogen in the cell gas to reduce the hydrogen in the vent to 5 percent, or a safe limit, is shown in Figure A-7.

The heat capacity of the dilution air is small compared with that of the chlorine and it is therefore assumed that the dilution air has no measurable effect on the temperature or pressure of the chlorine system. The point of entrance of the dilution air does, however, have an effect on the amount of chlorine in the blow gas. If the dilution air is added at or before the entrance to the final condenser such that equilibrium conditions can be assumed, doubling the inerts by adding dilution air will double the weight of chlorine in the blow gas (the percentage of chlorine will be unchanged). The weight of chlorine in the blow gas will increase but will not be quite doubled as is the case, for example, if the dilution air is added at or just before the exit of the final

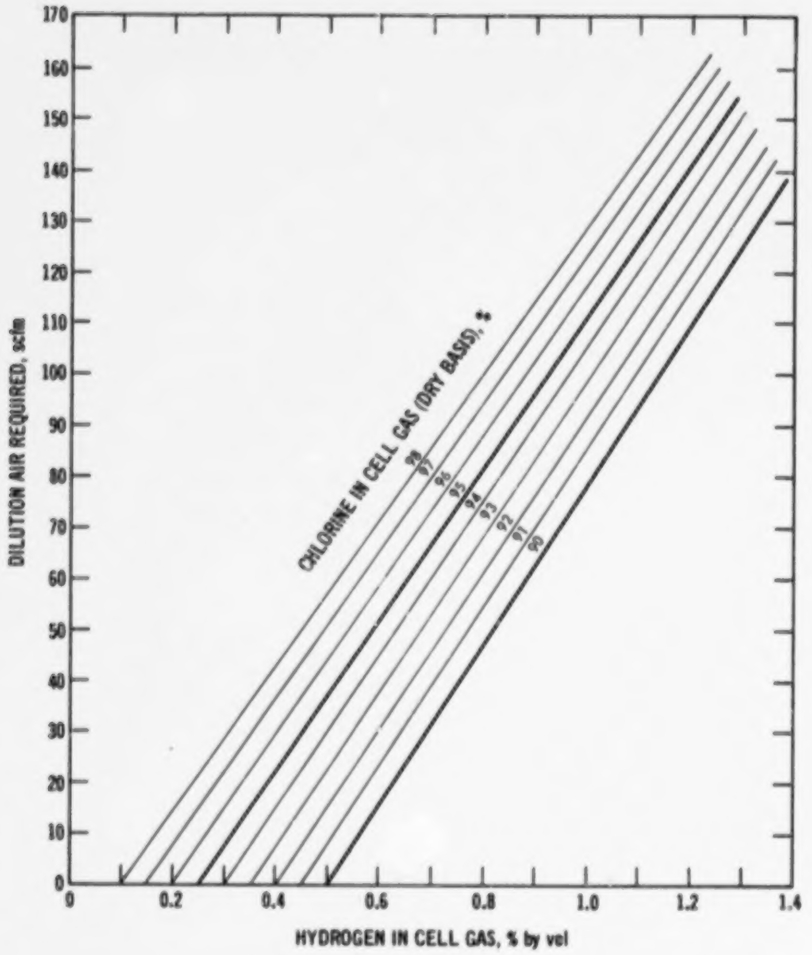


Figure A-7. Dilution air required (per 100 tons/day chlorine as cell gas) to reduce hydrogen in blow-gas absorber vent to 5% by volume (assume 0° C and 14.696 psia).

condenser. There will be no increase in chlorine if dilution air is added at the inlet to the blow-gas absorber. These variables in operating conditions have been included in one curve of Figure A-8, showing the chlorine that occurs in the blow gas with the various amounts of air dilution required to limit hydrogen in the absorber vent to 5 percent. Equilibrium conditions have been assumed in Figure A-8 but, as previously stated, the chlorine in the blow gas will be somewhat less if it is added just before the exit of the final condenser rather than at or before the entrance to the final condenser.

The percentage of chlorine in blow gas will vary considerably with operating conditions as noted. An average range is 20 to 50 percent.

The rate of potential or actual chlorine emissions in the blow gas will also vary with operating conditions. The potential emissions as weight per day will increase with percentage of chlorine in the blow gas, percentage of inerts in the cell gas, air dilution if added before the exit of the final condenser, and plant capacity. An average range for diaphragm cells is 1 to 5 tons of chlorine in blow gas per 100 tons of chlorine liquefied. Similarly, the average range for mercury cells is 2 to 8 tons of chlorine in blow gas per 100 tons liquefied.

EXAMPLE:

ASSUME 95.5% Cl_2 AND 0.4% H_2 IN CELL GAS AND 25% Cl_2 IN BLOW GAS. FROM ①② DILUTION AIR TO REDUCE H_2 IN BLOW-GAS ABSORBER VENT TO 5% IS 26 scfm/100 tons Cl_2 AS CELL GAS AND Cl_2 IN BLOW GAS BECOMES 1.75 ORIGINAL WEIGHT; FROM ③④ Cl_2 IN BLOW GAS WITHOUT AIR DILUTION = 1.6 tons; WITH AIR DILUTION, 1.75 x 1.6 = 2.8 tons.

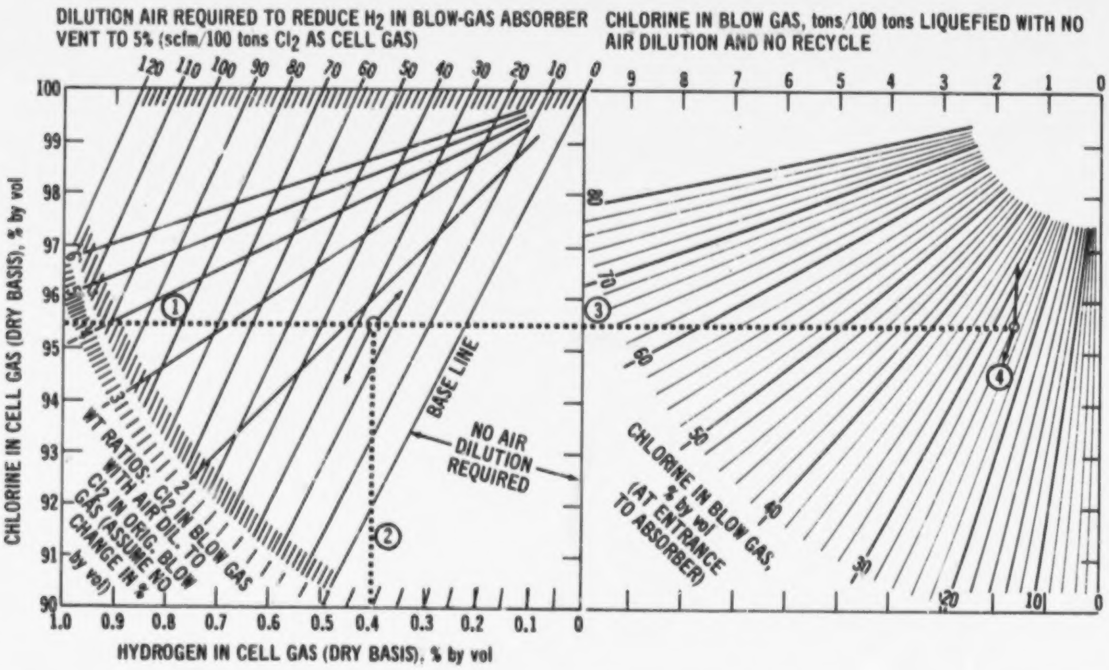


Figure A-8. Effect of air dilution on chlorine loss with blow gas (assume no chlorine recycle).

APPENDIX B. SAMPLING AND ANALYTICAL TECHNIQUES

The sampling and analytical techniques described were used by the National Air Pollution Control Administration to conduct source tests on four chlor-alkali plants. The analytical procedures are based on methods described in the literature and by manufacturers of chlorine and caustic.

DETERMINATION OF CHLORINE IN STACK GAS

This method is intended for the determination of gaseous chlorine in stack-gas samples. Chlorine is collected in an evacuated 2-liter flask and reacted with sodium hydroxide to form sodium hypochlorite. Because of the large variation in chlorine concentration in stack gas before and after scrubbers, two methods of analysis are used. Samples collected before the scrubber usually contain percentage quantities of chlorine and are analyzed by the Volhard Titration following reduction of the hypochlorite to chlorine by sodium arsenite. This method can be used to analyze for chlorine from percentage quantities down to about 5,000 ppm when 0.1 N reagents are used. Outlet samples after the scrubber usually contain ppm quantities and are analyzed by the ortho-tolidine method. Chlorine reacts under acid conditions (optimum pH 1.2) with ortho-tolidine to form the yellow holoquinone of ortho-tolidine dihydrochloride and is determined spectrophotometrically at 490 mμ. The color developed is proportional to the amount of chlorine present, and Beers' law is obeyed in the concentration range of 0 to 7 mg chlorine per liter.

Reagents

All chemicals used must be ACS analytical-reagent grade.

Water

Doubly distilled or deionized-distilled water.

Nitrobenzene

ACS reagent grade.

Ferric Indicator

Dissolve 28 grams of ferric ammonium sulfate, $FeNH_4(SO_4)_2 \cdot 12H_2O$, in 90 ml of hot water. Cool, filter, add 10 ml of concentrated nitric acid, and dilute to 100 ml in a volumetric flask. Use 1 to 3 ml of indicator per titration.

Nitric Acid (8 N)

Prepare NO_X-free nitric acid by adding 50 ml of concentrated nitric acid to 50 ml of distilled water and boil in a conical flask until the solution is colorless.

Sodium Chloride Solution (0.1 N) (Primary Standard)

Prepare a 0.1 N solution of sodium chloride by accurately weighing 5.846 grams of reagent-grade NaCl that has been dried at 120° C for 2 hours. Dissolve in distilled water and dilute to 1 liter in a volumetric flask.

Standard Silver Nitrate Solution (0.1 N)

Dissolve 17.0 grams of dried $AgNO_3$ in distilled water that has been tested for the presence of chlorides and dilute to 1 liter. Transfer the solution to an amber glass-stoppered bottle. Protect the solution from exposure to direct sunlight when not in use. Standardize the silver nitrate solution against 30 to 40 ml of the 0.1 NaCl solution, according to the Volhard Titration as described under the analytical section. From the net volume of $AgNO_3$ used in the titration and the weight of chloride present in the 30- to 40-ml sample used in standardization, compute the chlorine titer of the solution. One ml of 0.1 silver nitrate is equal to 0.003545 gram of chlorine or chloride.

Ammonium Thiocyanate (0.1 N)

Dissolve 8 grams of ammonium thiocyanate in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Determine the titer of NH_4CNS solution as related to the $AgNO_3$ solution by: (1) measuring 30 to 40 ml of the 0.1 N $AgNO_3$ solution; (2) adding 2 ml of ferric ammonium sulfate indicator and 5 ml of nitric acid (1:1); and (3) titrating with the NH_4CNS solution until the reddish-brown endpoint appears. Shake vigorously during titration. The NH_4CNS titer must be determined before the $AgNO_3$ is standardized.

Sodium Arsenite (20%)

Dissolve 20 grams of sodium arsenite in 100 ml of distilled water. Store in a glass-stoppered reagent bottle.

Sodium Hydroxide (10%)

Dissolve 10 grams of sodium hydroxide in 100 ml of distilled water. Store in a tightly closed polyethylene bottle.

Sodium Hydroxide (1 N)

Dissolve 40 grams of sodium hydroxide in 1 liter of distilled water. Store in a tightly closed polyethylene bottle. Use when ppm concentrations of chlorine and CO_2 are expected.

Ortho-Tolidine Dihydrochloride Solution (0.134%)

Dissolve 1.34 grams of ortho-tolidine dihydrochloride in 500 ml of distilled water. Add this solution, with constant stirring, to 500 ml of a mixture of distilled water (350 ml) and concentrated HCl (150 ml). Store in an amber, glass-stoppered bottle. This reagent is stable for 6 months.[28]

Apparatus

Flasks

Two-liter, pyrex, round-bottom flasks with sleeve and accompanying three-way stopcock with T-bore. The T-bore has a cone for the vertical leg and a ball and socket for the horizontal legs (Figure B-1).

Vacuum System

The vacuum system consists of a vacuum pump capable of pumping 0.1 cfm at 27 in. Hg vacuum, or more, connected by a quick connect to a vacuum gauge capable of measuring vacuum pressure with an accuracy of 0.25 in. Hg (Figure B-2).

Thermometer

Weston thermometer, range 25 to 125° F, 5-in. stem.

Probe

(See Figure B-3).

Glass "L"

Connects three-way stopcock to probe (Figure B-1).

Variable Transformer

Rated at 7.5 amps, 0 to 135 volts.

Glass Wool

One-fourth pound fine glass wool.

Dispenser (NaOH)

A 100-ml round-bottom flask, modified with a Teflon stopcock and ball-joint extension (Figure B-4).

Burettes

50 ml.

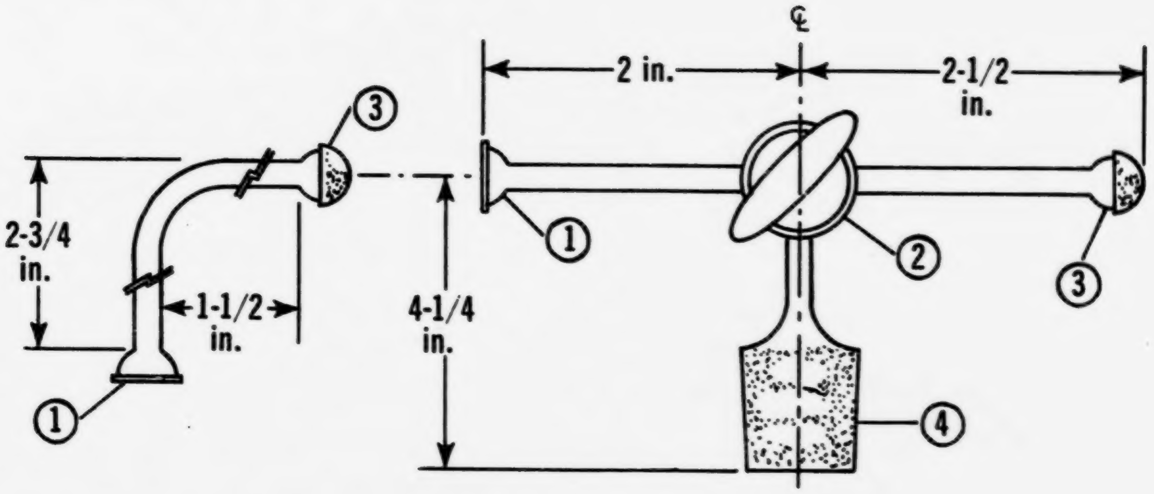
Spectrophotometer

This instrument should be capable of measuring optical density at 490 mμ in 0.5-in. absorbance cells, or at 440 mμ in 1-in. absorbance cells.

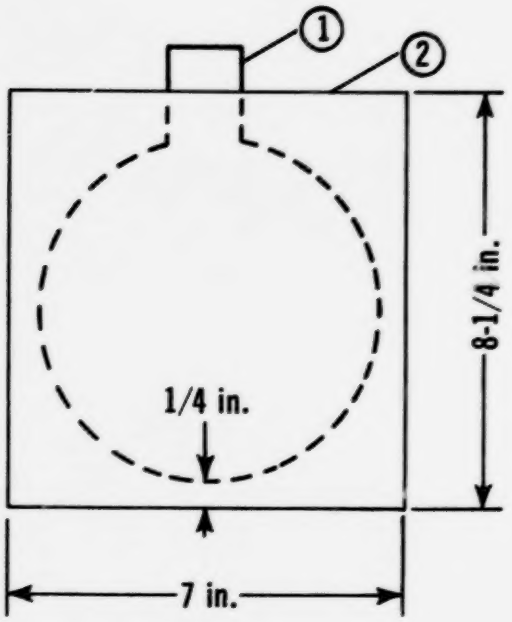
Analytical Procedures

Collection of Samples

Emission sources containing chlorine are sampled in quadruplicate by a grab-sampling technique using an evacuated 2-liter flask. The equipment developed and used by the Public Health Service is shown in Figure B-1.


℄
2 in.
2-1/2 in.
2-3/4 in.
1-1/2 in.
4-1/4 in.
①
②
③
④

1. GROUND-GLASS SOCKETS–§ NO. 12/5, PYREX.
2. STOPCOCK–THREE-WAY, T-BORE, ₸, PYREX, 2-mm BORE, 8-mm OD
3. GROUND-GLASS SOCKET–§ NO. 12/5.
4. GROUND-GLASS CONES–STANDARD TAPER, ₸ SLEEVE NO. 24/40.


①
②
8-1/4 in.
1/4 in.
7 in.

1. BOILING FLASK - 2-liter, ROUND-BOTTOM, SHORT-NECK, WITH ₸ SLEEVE NO. 24/40.
2. URETHANE FOAM ENCASEMENT.

Figure B-1. Three-way stopcock, "L", and flask.

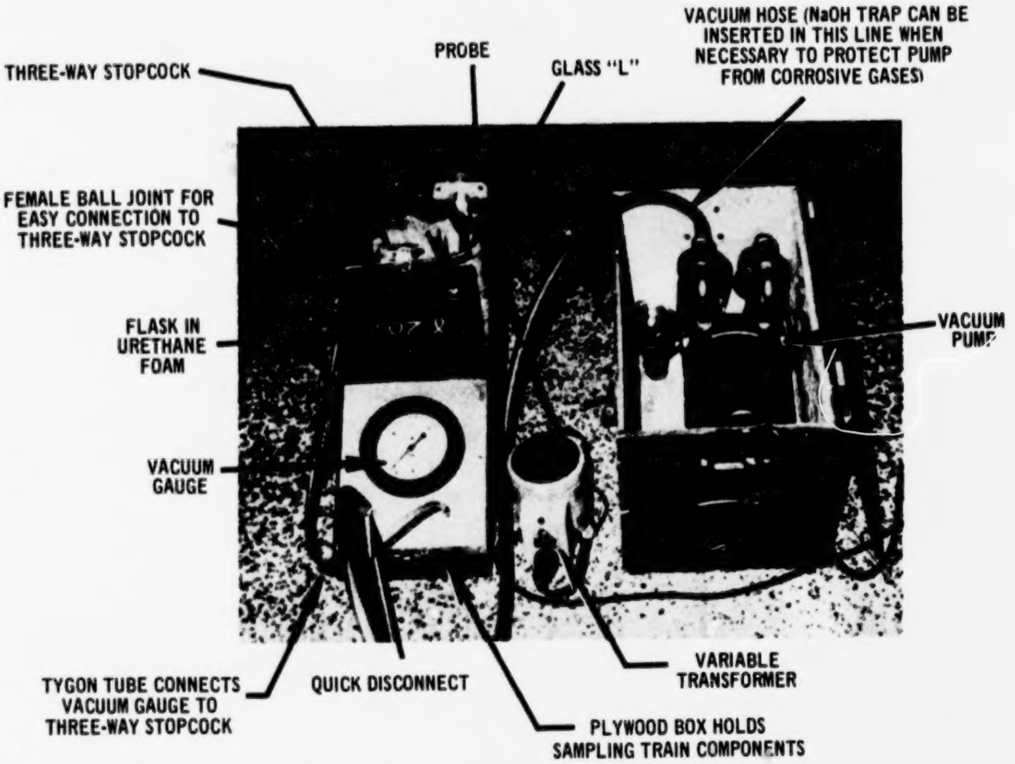

THREE-WAY STOPCOCK
PROBE
GLASS "L"
VACUUM HOSE (NaOH TRAP CAN BE INSERTED IN THIS LINE WHEN NECESSARY TO PROTECT PUMP FROM CORROSIVE GASES)
FEMALE BALL JOINT FOR EASY CONNECTION TO THREE-WAY STOPCOCK
FLASK IN URETHANE FOAM
VACUUM PUMP
VACUUM GAUGE
TYGON TUBE CONNECTS VACUUM GAUGE TO THREE-WAY STOPCOCK
QUICK DISCONNECT
VARIABLE TRANSFORMER
PLYWOOD BOX HOLDS SAMPLING TRAIN COMPONENTS

Figure B-2. Chlorine-sampling apparatus.

A 2-liter round-bottom flask encased in urethane foam and equipped with a three-way stopcock is connected to the probe via a glass "L". A wad of glass wool is inserted into the probe to minimize the amount of particulates entering the flask. A 500-ml wash bottle filled with a saturated caustic solution is placed in the line before the vacuum pump to protect it from corrosive gases (not shown in Figure B-2). The stem of a dial thermometer is inserted into the urethane foam adjacent to the flask.

The following procedure is used for the collection of samples. Connect the female ball-joint of the stopcock to the vacuum gauge and pump. Insert the sampling probe into the stack, turn on the vacuum pump, and purge stack gas through the stopcock. If condensation is observed in the stopcock, heat the probe by applying sufficient voltage to the probe heating element with the variable transformer. Turn the stopcock so that the vacuum pump and vacuum gauge are connected with the flask. Evacuate the flask to at least 25 inches of mercury vacuum. Disconnect the vacuum pump line at the quick disconnect (i.e., close the line to the vacuum gauge) and accurately measure the vacuum in the flask. Turn the three-way stopcock so that the flask is connected to the probe and vacuum gauge. Allow the flask to fill with a sample of stack gas until there is little or no vacuum left; however, avoid pressurizing the flask, a condition that is possible if stack pressure exceeds atmospheric pressure. If the flask takes longer than 15 seconds to fill, the glass wool filter is plugging and should be replaced. Measure precisely the final vacuum in the flask. Turn the three-way stopcock so that the flask is closed. Record the flask temperature indicated by the dial thermometer. Disconnect the flask and attach the burette to

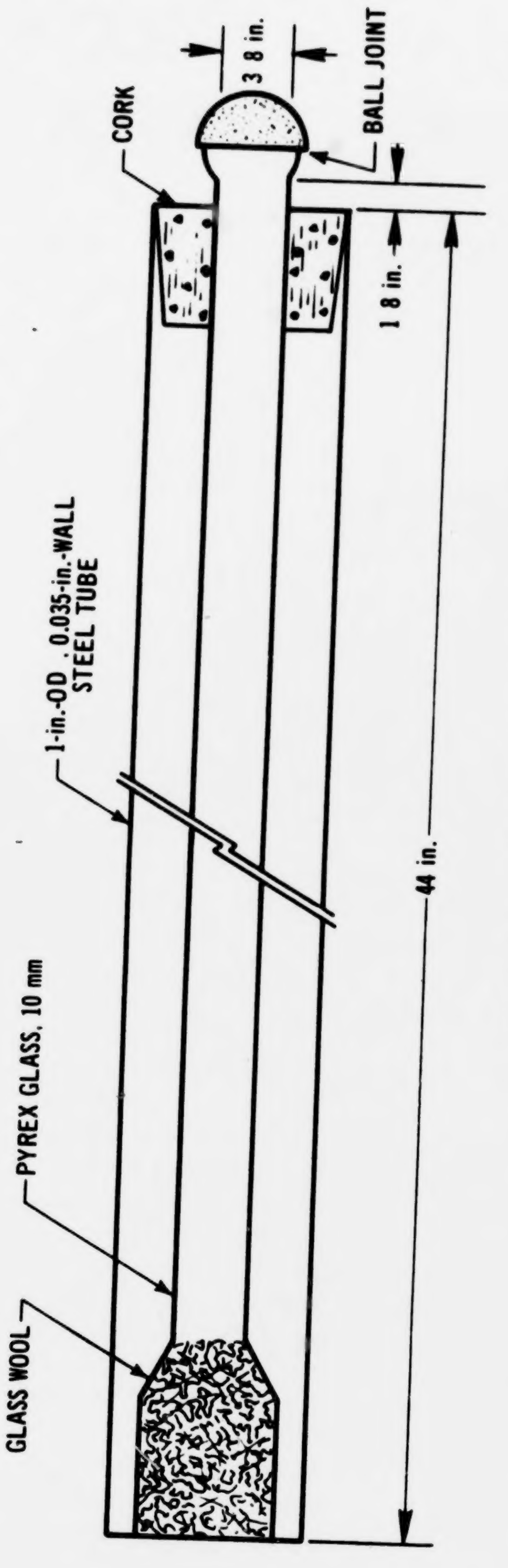

GLASS WOOL
PYREX GLASS, 10 mm
1-in.-OD , 0.035-in.-WALL STEEL TUBE
CORK
BALL JOINT
3 8 in.
1 8 in.
44 in.

Figure B-3. Probe for sampling chlorine.

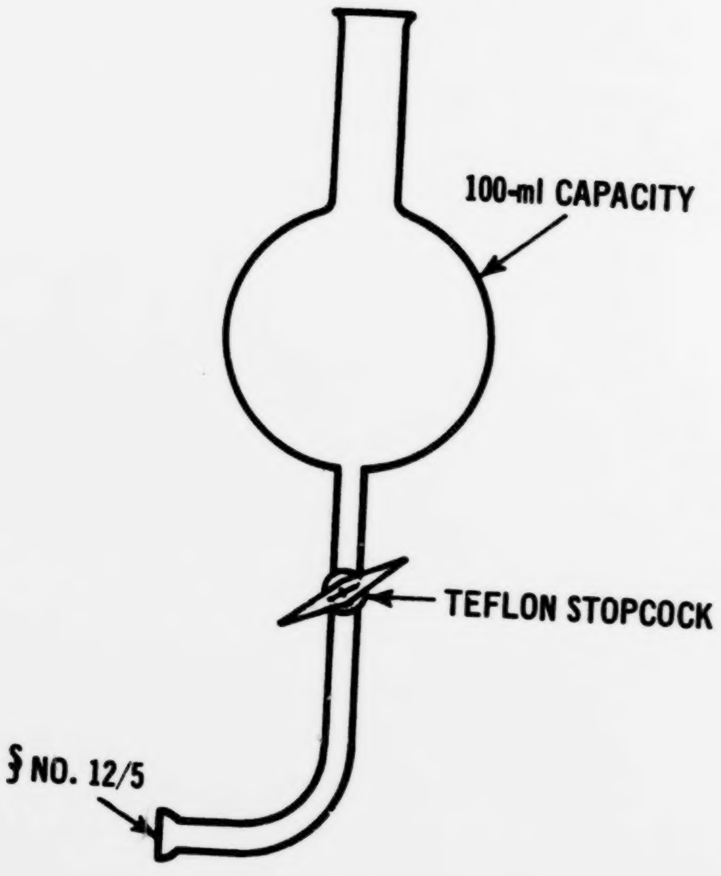


Figure B-4. Burette for adding NaOH.

the female ball-joint of the stopcock. Add approximately 50 ml of 10 percent sodium hydroxide to the burette when chlorine and carbon dioxide concentrations are expected to exceed 1 percent, and 50 ml of 1N NaOH for 1 percent or less. Open the burette stopcock, and slowly open the three-way stopcock to the burette. Because the NaOH solution readily absorbs chlorine, there is no difficulty in adding sufficient reagent to absorb all the chlorine present. The quantity and strength of NaOH should be adjusted to the amount of chlorine and CO_2 anticipated in the stack gas. Turn the stopcock so that the flask is closed. Shake the flask for 1 minute to ensure complete reaction of the NaOH with the chlorine. Record the data taken on a sheet such as that shown in Figure B-5.

Sample Preparation

Transfer the sample solution from the collection flask into a graduated cylinder. Wash the flasks three times with distilled water and add to the graduated cylinder. Adjust the solution to a known volume and transfer to a polyethylene container.

Analysis

Since there are two procedures for analyzing chlorine in stack-gas samples (i.e., for Cl_2 concentrations 0.5 percent or more and for Cl_2 concentrations less than 0.5 percent), each analytical method will be described separately.

Date____________________

Plant____________________

Operating conditions____________________

Sample collected by____________________

Run number____________________

Field data

Flask number				
Volume of flask less correction (V_f), ℓ.				
Pressure before sampling (P_i), in. of Hg				
Pressure after sampling (P_f), in. of Hg				
Flask temperature (T_f), °R				
Stack gas flow rate (Q), scfm				

Remarks

Figure B-5. Data sheet.

Method A: modified Volhard Titration for Cl_2 concentrations of 0.5 percent or more—Pipet an aliquot of the hypochlorite solution into a 250-ml Erlenmeyer flask. Add 50 ml of distilled water and 5 ml sodium arsenite solution. Swirl to mix and add 5 ml of nitric acid solution (1:1). Mix thoroughly. Omit this step when standardizing the silver nitrate against the standard sodium chloride solution.

Add 0.1 N $AgNO_3$ from a burette until it is in excess. Near the equivalence point, the silver chloride precipitate will coagulate. When coagulation occurs, add 5 ml of $AgNO_3$ in excess. Add 1 to 3 ml nitrobenzene to form an oily coat on the particles of AgCl and prevent reaction with the thiocyanate or, alternately, filter off the AgCl precipitate. Add 2 ml of indicator solution, swirl to mix, and titrate with thiocyanate until the first appearance of the reddish-brown $[Fe(CNS)_6]^{-3}$ complex. The color should last at least 1 minute with vigorous shaking. Determine the net volume of $AgNO_3$ consumed.

Calculations.

Compute the number of grams of chlorine present in the sample by the following equation:

$$X = \text{ml } AgNO_3 (T)(F) \qquad \text{(B-1)}$$

where

T = chlorine titer of standard $AgNO_3$

X = grams of chlorine

$$F = \frac{\text{total volume of sample, ml}}{\text{aliquot volume, ml}}$$

Calculate the liters of chlorine in the sample by the following equations:

$$\text{liters chlorine} = \frac{\text{g Cl} \times 22.4 \text{ liters/mole}}{71 \text{ g/mole}} \qquad \text{(B-2)}$$

71 = molecular weight Cl_2

22.4 liters/mole = gram-molecular volume at 32° F

Calculate the ppm chlorine in the sample by the following equation:

$$\text{ppm chlorine} = \frac{\text{liters of chlorine} \times 10^6}{\text{liters of gas sampled}} \qquad \text{(B-3)}$$

$$\text{Volume of gas samples} = \frac{(530^\circ \text{ R})\, V_f\, (P_f - P_i)}{29.92 \text{ in. Hg}(T_f)}$$

V_f = flask volume, liters

P_f = final flask pressure, in. Hg

P_i = initial flask pressure, in. Hg

T_f = flask temperature, °R

Method B: Ortho-tolidine The ortho-tolidine method is used to analyze scrubber outlet samples, in which ppm concentrations of chlorine are encountered. Pipet an aliquot of the sample into a 100-ml volumetric flask, neutralize with nitric acid, add 2 ml of ortho-tolidine reagent, and dilute to the mark with distilled water. Prepare a blank consisting of 2 ml of ortho-tolidine reagent and distilled water in a 100-ml volumetric flask. Using the blank, set the spectrophotometer at zero absorbance at 440 mμ. Read the absorbance of the sample in 0.5-inch absorbance cells within 5 minutes after the addition of the ortho-tolidine reagent.

Read the number of milligrams of chlorine present from a previously prepared calibration curve made by plotting absorbance versus milligrams of chlorine. Calculate the concentration of chlorine in ppm in the same manner as previously stated.

Preparation of Calibration Curve–Hypochlorite solutions for calibration purposes can be prepared by bubbling chlorine gas through 0.1 N NaOH. Certain commercial solutions of hypochlorite can also be used, such as Zonite (Zonite Products Corporation).* Zonite contains approximately 1 percent available chlorine.[31] Standardize the hypochlorite solution by adding an aliquot of the solution to an acid solution of potassium iodide. Titrate the equivalent amount of iodine released with standard sodium thiosulfate, using starch as an indicator.

Prepare a hypochlorite solution in which 1 ml contains approximately 1.0 mg available chlorine. Dilute 10 ml of this solution to 1 liter in a volumetric flask with distilled-deionized water. Standardize this solution by titrating as given above. Adjust the hypochlorite solution to contain 0.01 mg of chlorine per ml.

Pipet exactly 1, 5, 10, 20, 50, and 75 ml of the 0.01 mg/ml hypochlorite solution into 100-ml volumetric flasks, so that the solution will contain, respectively, 0.1, 0.5, 1.0, 2.0, 5.0, and 7.5 mg of chlorine per liter. Add 2 ml of the *o*-tolidine reagent to each flask and dilute to 100 ml with distilled-deionized water. Within 5 minutes after addition of the o-tolidine reagent, read the absorbance of the solution at 490 mμ in 0.5-inch absorbance cells, or at 440 mμ in 1-inch cells.

To prepare standards in the range of 0.01 mg/liter, dilute 100 ml of the original 0.01 mg/ml solution to 1 liter in a volumetric flask. This solution contains 0.001 mg/ml, or 1 mg/liter. Pipet 1, 5, 10, 20, 50, and 75 ml of this solution into 100-ml volumetric flasks, so that the flasks will contain, respectively, 0.01, 0.05, 0.1, 0.2, 0.5, and 0.75 mg of chlorine per liter. Add 2 ml of the o-tolidine reagent to each flask and dilute to 100 ml with distilled-deionized water. Within 5 minutes after addition of the o-tolidine reagent, read the absorbance of the solution at 440 mμ in 1-inch absorbance cells, or at 490 mμ in 0.5-inch absorbance cells.

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*Mention of commercial products or company names does not constitute endorsement by the Air Pollution Control Office or the Environmental Protection Agency.

Prepare a calibration curve by plotting absorbance versus concentration on rectangular graph paper.

Discussion of Procedures

The estimated error for the combined sampling and analytical procedure using the Volhard Titration is ± 7 percent for samples containing more than 0.05 percent chlorine. The precision of the analytical method is ± 2 percent on standard samples containing NaCl.

The usual volumetric errors are encountered with this method. Premature endpoints may occur if the NH_4CNS is not added dropwise near the equivalence point and the solution shaken before the next addition. The necessity of removing silver chloride by filtering or coating the precipitate (AgCl) with nitrobenzene has been emphasized. Interferring substances that form insoluble silver salts, and bivalent mercury, which forms a stable complex with the thiocyanate, must be absent from the sample.

The estimated error for combined sampling and analysis using the o-tolidine method is ± 7 percent in the concentration range of 1 to 7 mg/liter. Analyses of samples containing more than 7 mg chlorine/liter may be performed by taking an appropriate aliquot of the sample. Precision and accuracy of the o-tolidine method are greatest for samples containing about 1 mg/liter.

Distilled-deionized water free of chlorine should be used in all procedures where water is used. Nitrites and ferric compounds, when present, interfere with the analysis. For best results, the pH of the solution must be 1.3 during the contact time, and the chlorine concentration must not exceed 10 mg/liter.[23] Extreme care is required in preparing standards from hypochlorite solutions. Color comparisons should be made at the time of maximum color development. If the sample contains predominantly free chlorine as the hypochlorite, the maximum color appears almost instantaneously and begins to fade.[32] Samples containing combined chlorine (i.e., chloroamines) develop their maximum color within 3 minutes at 25° C and should be allowed to develop color in the dark.[32] If it can be shown that maximum color development occurs instantly, the absorbance of the samples and standards should be read either as quickly as possible or at a designated time following addition of the o-tolidine reagent. Absorbance readings can be taken within 5 minutes after addition of the o-tolidine reagent with no apparent color fading.

DETERMINATION OF CARBON DIOXIDE IN THE PRESENCE OF CHLORINE

Carbon dioxide and chlorine can be collected simultaneously in a 2-liter evacuated flask, reacted with sodium hydroxide to form sodium carbonate and sodium hypochlorite, and analyzed separately. Chlorine is determined by using the Volhard Titration of chloride, following reduction of the hypochlorite to chloride with sodium arsenite. Carbon dioxide, evolved from sodium carbonate upon acidification, is collected on ascarite and then determined gravimetrically. Carbonate-free reagents (sodium hydroxide, sodium arsenite) must be used if analyses for both chlorine and carbon dioxide are performed. The gravimetric method is applicable to the determination of carbon dioxide in the range of 0.3 to 25 percent by volume in stack gases in the presence of chlorine.

Reagents

All chemicals must be ACS analytical-reagent grade.

Water

Distilled-deionized water.

Sodium hydroxide (10%)

Prepare carbonate-free sodium hydroxide by dissolving 100 grams of NaOH in freshly boiled and cooled water and diluting to 1 liter.

Sodium arsenite (20%)

Dissolve 20 grams of carbonate-free sodium arsenite ($NaAsO_2$) in 100 ml of water or prepare from primary-standard-grade arsenic trioxide.

Ascarite

Eight to 20 mesh.

Apparatus

Drying tube

Glass drying tube with two ground-glass stopcocks. The tube is filled with ascarite and several grams of drierite.

Evolution apparatus

See Figure B-6.

Sampling equipment

Same as for chlorine.

Analytical Procedures

Collection of samples

Same as for chlorine

Cleanup

Same as for chlorine.

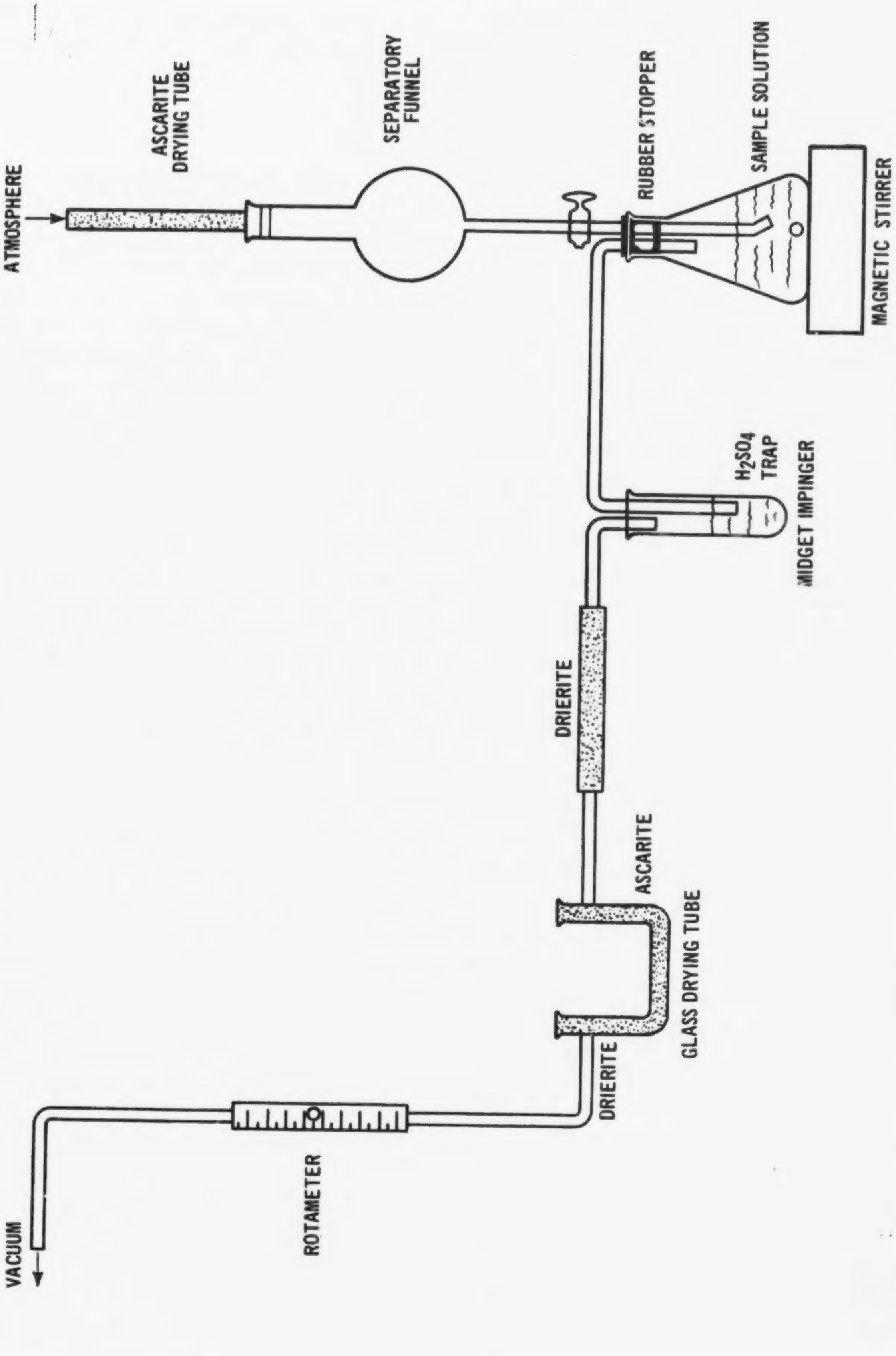

VACUUM
ROTAMETER
DRIERITE
GLASS DRYING TUBE
ASCARITE
DRIERITE
MIDGET IMPINGER
H_2SO_4 TRAP
MAGNETIC STIRRER
SAMPLE SOLUTION
RUBBER STOPPER
SEPARATORY FUNNEL
ASCARITE DRYING TUBE
ATMOSPHERE

Figure B-6. Apparatus for determination of carbon dioxide in presence of chlorine.

Analysis

Transfer an aliquot of the sample to a 100-ml Erlenmeyer flask and add 10 ml of sodium arsenite (carbon-free) for prescrubber samples and 2 ml for outlet samples. Set up the apparatus as shown in Figure B-6. Place 20 ml of 1:1 HCl in the separatory funnel along with 5 drops of 0.1 percent methyl-red indicator and start the magnetic stirrer. Preweigh the glass drying tube containing ascarite and drierite to the nearest 0.1 mg and insert into the sampling line. Open the stopcocks to the drying tube, turn on the vacuum source, and open the separatory funnel stopcock. Adjust the flow to approximately 200 cc/min. and run the sample for 15 minutes. Shut off the vacuum and the drying tube stopcocks and remove the drying tube from the line. Carefully weigh the drying tube and determine the amount of CO_2 collected on the ascarite by subtracting the tare weight of the tube. A blank should also be run to determine the background CO_2 in the reagents. Using the aliquot factor, calculate the total weight of CO_2 in the sample.

Discussion of Procedures

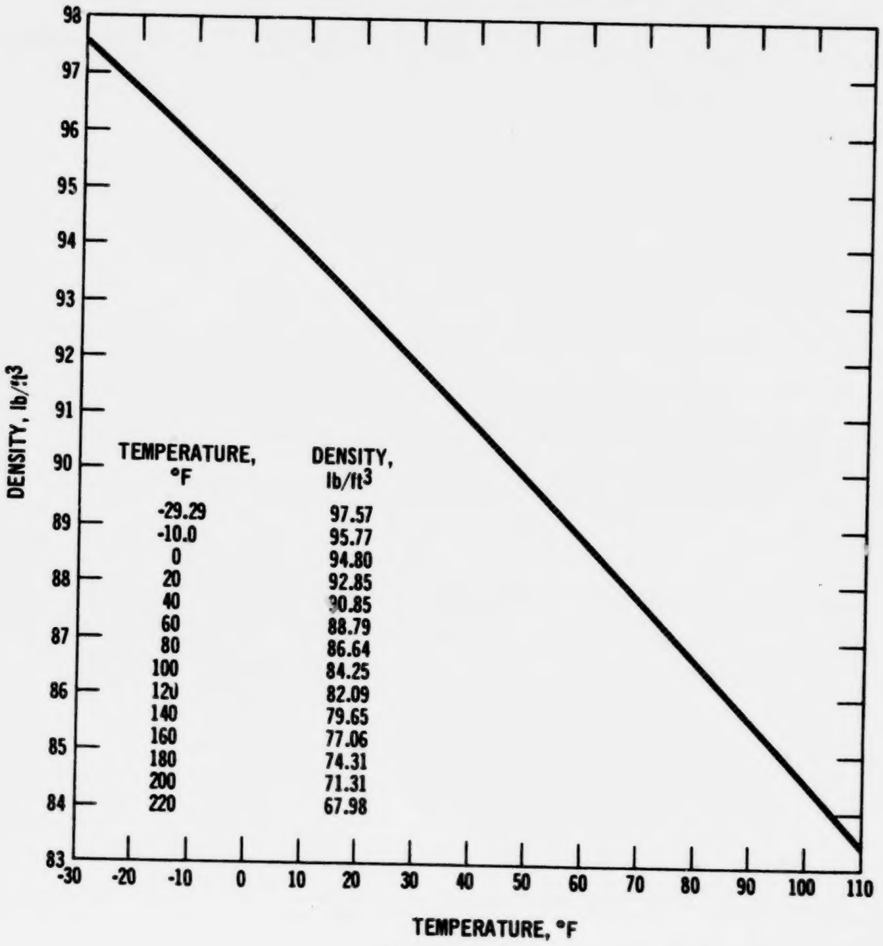
The evolution of carbon dioxide from sodium carbonate solutions has been applied to the measurement of CO_2 in stack gases containing large concentrations of chlorine. Reduction of the hypochlorite to chloride with arsenite prevents the formation of volatile hypochlorous acid upon acidification. The pH of the solution upon acidification should be less than 2 to ensure complete evolution of CO_2. Water vapor is removed in the sulfuric acid impinger and in the drierite drying tube and does not enter the glass drying tube. When exhausted, as indicated by the formation of white sodium carbonate, the ascarite should be replaced. Standard samples of sodium carbonate result in 99 percent recovery of CO_2 with no interference from the presence of chlorides produced from the reduction of hypochlorite.

APPENDIX C. PHYSICAL DATA

Some physical and chemical properties of chlorine, caustic soda, caustic potash, and sodium are given in Appendix C.

CHLORINE

Liquid chlorine is a clear amber-colored liquid about 1.5 times the density of water (see Figure C-1). At atmospheric pressure it has a boiling point of -29.29° F and is usually shipped in steel containers as a liquid under pressure. Wet chlorine gas or liquid is quite corrosive to all common metals. Gold, silver, platinum, and tantalum resist both wet and dry chlorine at temperatures less than 300° F. Titanium resists wet chlorine but is attacked by dry. In the manufacture of chlorine the wet gas is usually handled in chemical stoneware,



TEMPERATURE, °F	DENSITY, lb/ft^3
-29.29	97.57
-10.0	95.77
0	94.80
20	92.85
40	90.85
60	88.79
80	86.64
100	84.25
120	82.09
140	79.65
160	77.06
180	74.31
200	71.31
220	67.98

Figure C-1. Density of liquid chlorine.[33]

glass, porcelain, and certain plastics such as Haveg and polyesters. After the gas is dried it is compressed, liquefied, and stored in steel equipment. The use of steel for handling dry chlorine is usually limited to temperatures of about 212° F and less. Nickel, Hastelloy C, Monel, and types 304 and 316 stainless steel may be used at temperatures higher than this.

Minor leaks of gaseous or liquid chlorine are potentially hazardous. Expansion of the liquid or gas in the vicinity of the leak will condense moisture from the air, rapidly increase the corrosion rate, and thereby increase the extent of leakage to the atmosphere. One pound of the liquid will rapidly expand to about 460 times its liquid volume, occupying 5 cubic feet. The gas is greenish-yellow and about 2.5 times as heavy as air. It tends, therefore, to flow to the floor or lower levels of a building.

Chlorine is nonexplosive, noncombustible, and a nonconductor of electricity. When chlorine is dissolved in pure water, weak solutions of hydrochloric and hypochlorous acid are formed. The water solution is an oxidizing agent of moderate strength. The maximum solubility of chlorine is approximately 1 percent at 49.3° F; it is insoluble in boiling water. For the solubility of chlorine in water, see Table C-1. At temperatures below 49.3° F, chlorine hydrate ($Cl_2 \cdot 8H_2O$), usually referred to as "chlorine ice," may crystallize.

Purity of Commercial Chlorine

Commercial liquid chlorine averages about 99.4 percent chlorine and contains in solution solid, liquid, and gaseous impurities in small amounts. The following are approximate:

1. Gaseous impurities (largely due to air padding of tank cars): $CO_2 = 0.5$ to 0.7 percent by volume; $O_2 = 0.04$ to 0.1 percent by volume; and $N_2 =$ 0.07 to 0.3 percent by volume.

2. Liquid impurities: 40 ppm total, largely carbon tetrachloride, chloroform, and chloroethanes; and 40 ppm bromine, usually not considered an impurity since it reacts chemically very much like chlorine.

3. Solid impurities: 100 ppm total, largely hexachloroethane and ferric chloride.

Solid impurities may be troublesome since they tend to deposit in orifices, valves, and control instruments. When chlorine is used at low rates, thus requiring small mechanical clearances or orifices, as in water purification, glass wool filters are commonly used to remove a considerable amount of the solid impurities. Moreover, higher purity chlorine is frequently used. By fractional distillation of commercial chlorine, solid impurities can be reduced to about 25 ppm.

Atomic and Molecular Properties

Atomic symbol:	Cl
Atomic weight:	35.457

Table C-1. SOLUBILITY OF CHLORINE IN WATER AS A FUNCTION OF PARTIAL PRESSURE AND TEMPERATURE[34]

Partial pressure of Cl_2, mm Hg	Solubility, g of Cl_2/liter											
	0° C	10° C	20° C	30° C	40° C	50° C	60° C	70° C	80° C	90° C	100° C	110° C
5	0.488	0.451	0.438	0.424	0.412	0.398	0.383	0.369	0.351	0.339	0.326	0.316
10	0.679	0.603	0.575	0.553	0.532	0.512	0.492	0.470	0.447	0.431	0.415	0.402
30	1.221	1.024	0.937	0.873	0.821	0.781	0.743	0.704	0.671	0.642	0.627	0.598
50	1.717	1.354	1.210	1.106	1.025	0.962	0.912	0.863	0.815	0.781	0.747	0.722
100	2.79	2.08	1.773	1.573	1.424	1.313	1.228	1.149	1.085	1.034	0.987	0.950
150	3.81	2.73	2.27	1.966	1.754	1.599	1.482	1.382	1.294	1.227	1.174	1.137
200	4.78	3.35	2.74	2.34	2.05	1.856	1.706	1.580	1.479	1.396	1.333	1.276
250	5.71	3.95	3.19	2.69	2.34	2.09	1.914	1.764	1.642	1.553	1.480	1.413
300	–	4.54	3.63	3.03	2.61	2.31	2.10	1.932	1.793	1.700	1.610	1.542
350	–	5.13	4.06	3.35	2.86	2.53	2.28	2.10	1.940	1.931	1.736	1.661
400	–	5.71	4.48	3.69	3.11	2.74	2.47	2.25	2.08	1.965	1.854	1.773
450	–	6.26	4.88	3.98	3.36	2.94	2.64	2.41	2.22	2.09	1.972	1.880
500	–	6.85	5.29	4.30	3.61	3.14	2.80	2.55	2.35	2.21	2.08	1.986
550	–	7.39	5.71	4.60	3.84	3.33	2.97	2.69	2.47	2.32	2.19	2.09
600	–	7.97	6.12	4.91	4.08	3.52	3.13	2.83	2.59	2.43	2.29	2.19
650	–	8.52	6.52	5.21	4.32	3.71	3.29	2.97	2.72	2.55	2.41	2.28
700	–	9.09	6.90	5.50	4.54	3.89	3.44	3.10	2.84	2.66	2.50	2.37
750	–	9.65	7.29	5.80	4.77	4.07	3.59	3.23	2.96	2.76	260	2.47
800	–	10.21	7.69	6.08	4.99	4.27	3.75	3.37	3.08	2.87	2.69	2.56
900	–	–	8.46	6.68	5.44	4.62	4.04	3.63	3.30	3.08	2.89	2.74
1000	–	–	9.27	7.27	5.89	4.97	4.36	3.88	3.53	3.28	3.07	2.91
1200	$Cl_2 \cdot 8H_2O$ separates		10.84	8.42	6.81	5.67	4.92	4.37	3.95	3.67	3.43	3.25
1500	–	–	13.23	10.14	8.05	6.70	5.76	5.09	4.58	4.23	3.95	3.74
2000	–	–	17.07	13.02	10.22	8.38	7.14	6.26	5.63	5.17	4.78	4.49
2500	–	–	21.0	15.84	12.32	10.03	8.48	7.40	6.61	6.05	5.59	5.25
3000	–	–	–	18.73	14.47	11.70	9.83	8.52	7.54	6.92	6.38	5.97
3500	–	–	–	21.7	16.62	13.38	11.22	9.65	8.53	7.79	7.16	6.72
4000	–	–	–	24.7	18.84	15.04	12.54	10.76	9.52	8.65	7.94	7.42
4500	–	–	–	27.7	20.7	16.75	13.88	11.91	10.46	9.49	8.72	8.13
5000	–	–	–	30.8	23.3	18.46	15.26	13.01	11.42	10.35	9.48	8.84

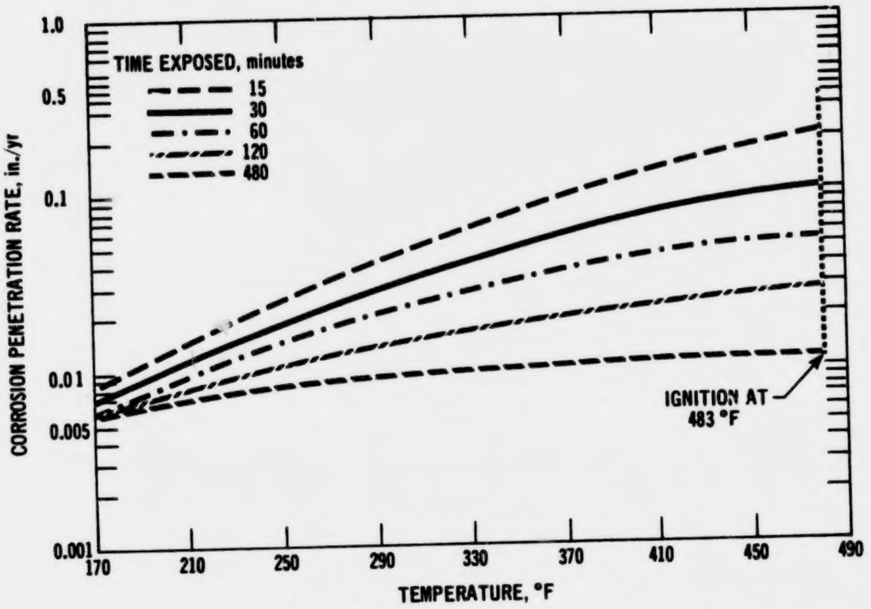


Figure C-2. Effect of temperature on corrosion of mild steel by chlorine.[35]

Atomic number:	17 (Number of protons within the atomic nucleus.)
Molecular symbol:	Cl_2
Molecular weight:	70.906

Chemical Properties

Valence: Usually forms univalent compounds but can combine with a valence of 3, 4, 5, or 7.

Chemical Reactions: Nonflammable; like oxygen, however, it is capable of supporting the combustion of certain substances. Many organic chemicals react readily with chlorine, sometimes with explosive violence.

The rate of chlorine corrosion of most metals increases rapidly with temperature, particularly if the metal is finely divided or is in wire, powder, or sponge form. Dry chlorine reacts with aluminum, arsenic, gold, mercury, selenium, tellurium, tin, and titanium. Potassium and sodium will burn in chlorine at most temperatures, and steel will ignite at 483° F (see Figure C-2).

When in finely divided form, antimony, arsenic, bismuth, boron, copper, iron, phosphorus, and certain of their alloys will ignite spontaneously in chlorine. Mixtures of chlorine and hydrogen can react with explosive violence, the lower limit being about 5 percent H_2 (see Figure A-4). Chlorine removes hydrogen from some of its compounds, as in its reaction with hydrogen sulfide to form hydrochloric acid and sulfur. It reacts with ammonia and ammonium compounds to form various chloroamines. Under proper conditions nitrogen trichloride, which is highly explosive, is formed.

The reactions of chlorine with organic compounds are similar to those with inorganic compounds, with hydrogen chloride and chlorinated derivatives being formed. Some of these reactions, including those with hydrocarbons, alcohols, and ethers, can be explosive, and care should be used in selecting the proper methods and procedures for these reactions. For the solubility of chlorine in selected solvents, see Figure C-3.

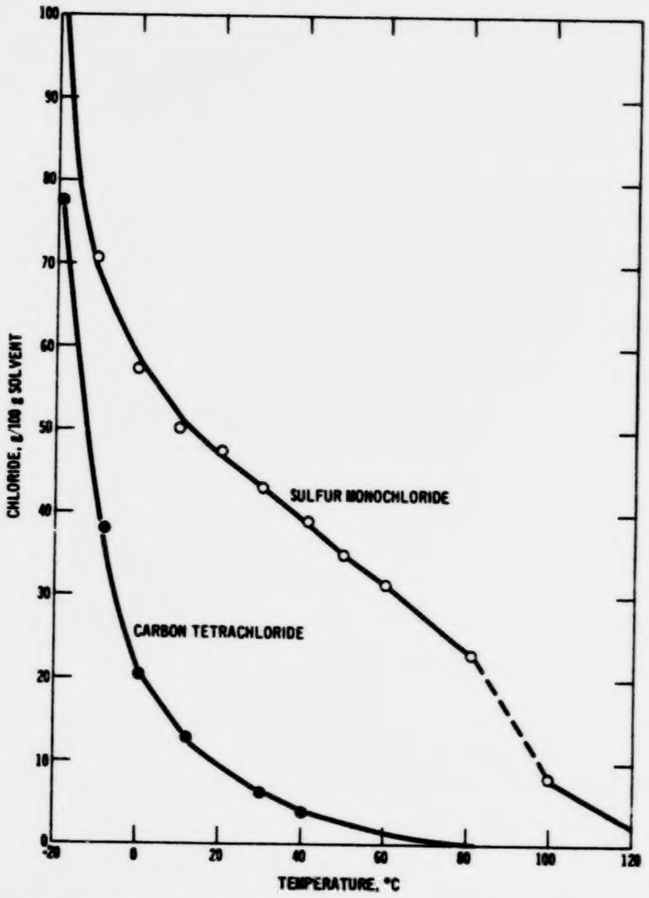


Figure C-3. Solubility of chlorine in selected solvents at atmospheric pressure.[34]

Physical Properties [35]

Boiling point

-29.29° F at 1 atmosphere pressure (14.696 psia)

Critical properties

Critical density: 35.77 lb/ft^3 or 0.573 g/cc. Mass of unit volume of chlorine at the critical pressure and temperature.

Critical pressure: 1,118.4 psia (76.1 atm). Pressure at critical temperatures.

Critical temperature: 291.2° F (144° C). Temperature above which chlorine exists as a gas regardless of increase in pressure.

Critical volume: 0.02796 ft^3/lb (1.745 cc/g). Volume of unit mass of chlorine at the critical pressure and temperature.

Density

Dry gas: 0.2003 lb/ft^3 (0.003209 g/cc) at standard conditions.*

Saturated gas: 0.7537 lb/ft^3 (12.07 g/liter at 32° F (0° C).**

Liquid: 91.67 lb/ft^3 (1.468 g/liter at 32° F (0° C) (see Figure C-1).

Liquid: 88.79 lb/ft^3 (11.87 lb/gal) at 60° F (15.6° C). Pressure of liquid chlorine at 60° F is 85.61 psia.

Latent heat of vaporization

123.7 Btu/lb (68.7 gcal/g) at the boiling point of -29.29°F.

Melting point

-149.76°F (-100.98°C), temperature at which solid chlorine melts or liquid chlorine solidifies under 1 atmosphere pressure (14.696 psia).

Specific gravity

Gas: 2.482 (air = 1).

Liquid: 1.418 (at 0° C).

Specific heat*

Dry gas at constant pressure: 0.115 Btu/lb-° F at 15 psia between 50° F and 100° F. (C_p 8.28 + 0.0056T, where C_p is in cal/degree mol and T is in ° K for the range 273 to 2,000° K.

Dry gas at constant volume: 0.0848 Btu/lb-° F at 15 psia between 50° F and 100° F.

Liquid: 0.236 Btu/lb-° F at equilibrium between 0° F and 100° F.

$C_p/C_v = 1.355$; ratio of gas specific heat at constant pressure to specific heat at constant volume at 1 atm and 15° C.

Specific volume*

Dry gas: 4.992 ft^3/lb at standard conditions.*

Saturated gas: 1.327 ft^3/lb at 32° F.**

Liquid: 0.01091 ft^3/lb at 32° F.**

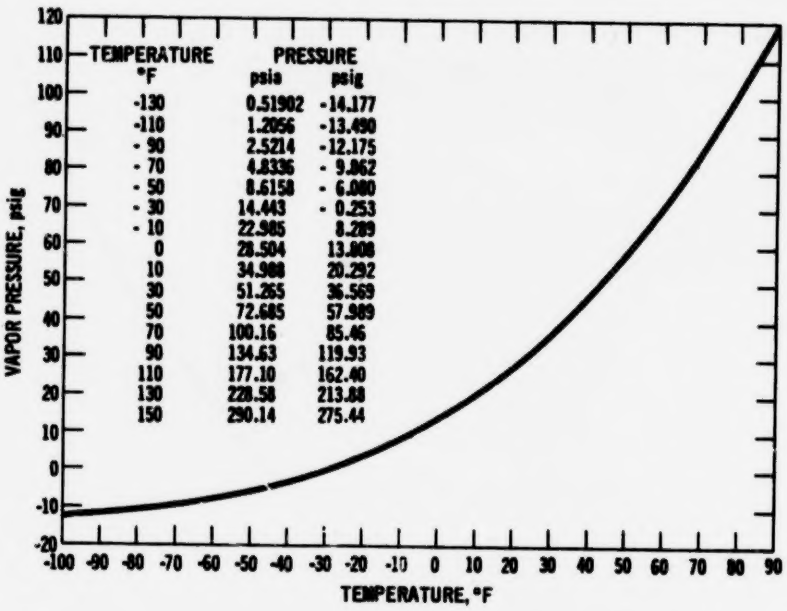
Vapor pressure*

At 32°F, vapor pressure is 3.617 atm, or 53.155 psia (see Figure C-4).

---

*Standard conditions are 32° F (0° C) and 14.696 psia (1 atm).

**Pressure of saturated gas and liquid chlorine at 32° F (0° F) is 53.155 psia (3.617 atm).



TEMPERATURE °F	PRESSURE psia	PRESSURE psig
-130	0.51902	-14.177
-110	1.2056	-13.490
- 90	2.5214	-12.175
- 70	4.8336	- 9.862
- 50	8.6158	- 6.080
- 30	14.443	- 0.253
- 10	22.985	8.289
0	28.504	13.808
10	34.988	20.292
30	51.265	36.569
50	72.685	57.989
70	100.16	85.46
90	134.63	119.93
110	177.10	162.40
130	228.58	213.88
150	290.14	275.44

Figure C-4. Vapor pressure of liquid chlorine.[35]

Viscosity

Gas at 20°C, 1.4 × 10^{-4} poises.

Volume in air

See Figure C-5.

CAUSTIC SODA[36]

Anhydrous caustic soda is a white, translucent solid having a crystalline structure. It is deliquescent and also absorbs carbon dioxide from the air, with the formation of sodium carbonate. It dissolves readily in water, with evolution of heat, to form a colorless solution. Viscosity increases rapidly with concentration.

Caustic soda, or sodium hydroxide, has the chemical formula, $NaOH$, a molecular weight of 40, and a specific gravity of $2.13_{4}^{15.5}$. It melts at 3.8° C and has a boiling point of 1,390° C. The latent heat of fusion is 40 cal/g and the heat of solution is 10.3 kcal/g mol at 22° C (463 Btu/lb). The solubility is 42 g/100 ml of water at 0° C and 347 g/100 ml of water at 100° C.

Freezing points of caustic soda solutions are shown in Figure C-6. Viscosities of solutions at various temperatures are shown in Figure C-7, and vapor pressures of solutions at various temperatures are shown in Figure C-8. Specific gravities of caustic solutions are shown in Table C-2.

Commercial caustic soda is most frequently shipped as a 50 percent solution, or it may be further concentrated to 73 percent. A dilution nomograph for caustic soda is given in Figure C-9. Solid caustic may be shipped in drums as such or as flake. Rayon-grade caustic may be made by

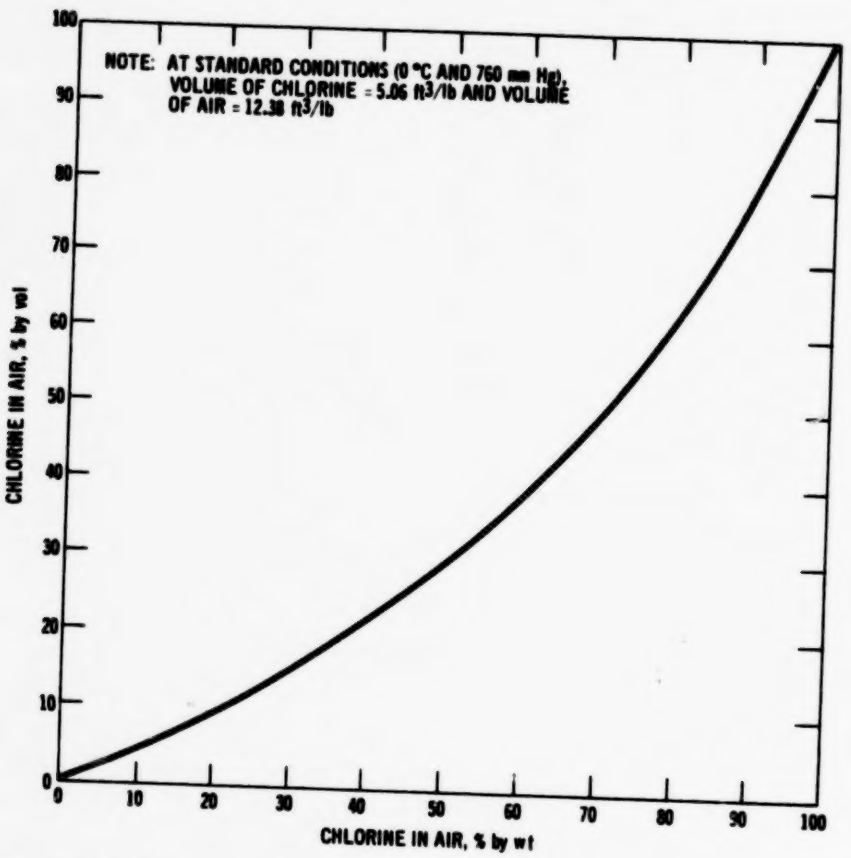


Figure C-5. Percent chlorine in air by volume versus percent by weight and weight of gas mixture at standard conditions.

further reducing the small content of salt and other impurities present in standard-grade caustic. High purity 50 percent caustic is produced in mercury cells directly without evaporation or purification.

CAUSTIC POTASH

Anhydrous caustic potash or potassium hydroxide is a white, translucent, crystalline solid with properties somewhat similar to those of caustic soda. In reaction with other chemicals, the products formed frequently differ from the properties of similar sodium chemicals. Caustic potash is therefore used in special cases for soaps, glass, textiles, and chemicals where the particular property of the product cannot be obtained by the use of the lower-priced caustic soda.

Potassium hydroxide (KOH) has a molecular weight of 56.1 and a density of $2.044_4^{15.5}$. It has a melting point of 360.4 to 367° C and a boiling point of 1,320 to 1,324° C. The heat of solution is 12.95 kcal/g mol at 21° C. The solubility is 97 g/100 ml of water at 0° C and 178 g/100 ml at 100° C.

The standard-grade caustic potash contains 90 percent KOH. A product having low iron and salt is produced having 85 percent KOH. Liquid grades

Table C-2. SPECIFIC GRAVITY OF CAUSTIC SODA SOLUTIONS AT 60° F BASED ON DILUTION OF 50 PERCENT STANDARD-GRADE CAUSTIC[37]

NaOH, % by wt.	% Na_2O	Sp. gr., 60° F/60° F	°Bé	°Twaddell	NaOH, g/liter	NaOH, lb/gal
2	1.55	1.023	3.3	4.6	20.5	0.17
4	3.10	1.045	6.2	9.0	41.8	0.35
6	4.65	1.067	9.1	13.6	63.9	0.53
8	6.20	1.090	12.0	18.0	87.2	0.73
10	7.75	1.111	14.6	22.4	111.1	0.93
12	9.30	1.130	17.1	26.8	135.6	1.13
14	10.85	1.156	19.6	31.2	161.8	1.35
16	12.40	1.178	21.9	35.8	188.5	1.57
18	13.95	1.201	24.3	40.2	216.2	1.80
20	15.50	1.223	26.4	44.6	244.5	2.04
22	17.05	1.245	28.5	49.0	274.0	2.28
24	18.60	1.267	30.6	53.4	304.0	2.53
26	20.15	1.289	32.5	57.8	335.0	2.79
28	21.70	1.311	34.4	62.0	367.0	3.06
30	23.25	1.332	36.1	66.4	399.5	3.34
32	24.80	1.356	38.1	71.2	434.0	3.62
34	26.35	1.378	39.8	75.6	468.0	3.91
36	27.90	1.400	41.5	79.9	504.0	4.20
38	29.45	1.420	42.9	84.0	540.0	4.50
40	31.00	1.438	44.3	87.6	576.0	4.80
42	32.55	1.457	45.6	91.4	612.0	5.11
44	34.10	1.476	46.7	95.1	649.0	5.42
46	35.65	1.495	48.0	98.9	688.0	5.74
48	37.20	1.514	49.3	103.0	727.0	6.07
50	38.75	1.532	50.3	106.3	767.0	6.39
52	40.30	1.552	51.6	110.3	807.0	6.73

contain 45 to 52 percent KOH, the lower strength product being more desirable for shipment in cold weather.

SODIUM

Sodium is a waxy, bright, silvery metal readily cut by a knife. In moist air it rapidly tarnishes, becoming dull grey. When sodium is exposed to the atmosphere over a long period, an amorphous skin of hygroscopic oxide forms on the metal. In atmospheric air the metal ignites at 115° C, but in very dry air ignition does not occur until the metal is near its boiling point. The flame of burning sodium has a characteristic yellow color. Pure sodium melts at 97.8° C and boils at 892° C. The density at 20° C is 0.971; a cubic foot of sodium weighs about 60.5 pounds. Sodium is soluble in liquid ammonia (26.6% at 22° C), molten caustic soda (6.5% at 800° C), fused sodium chloride (4.2% at 88° C), and in mixtures of sodium and calcium chlorides.

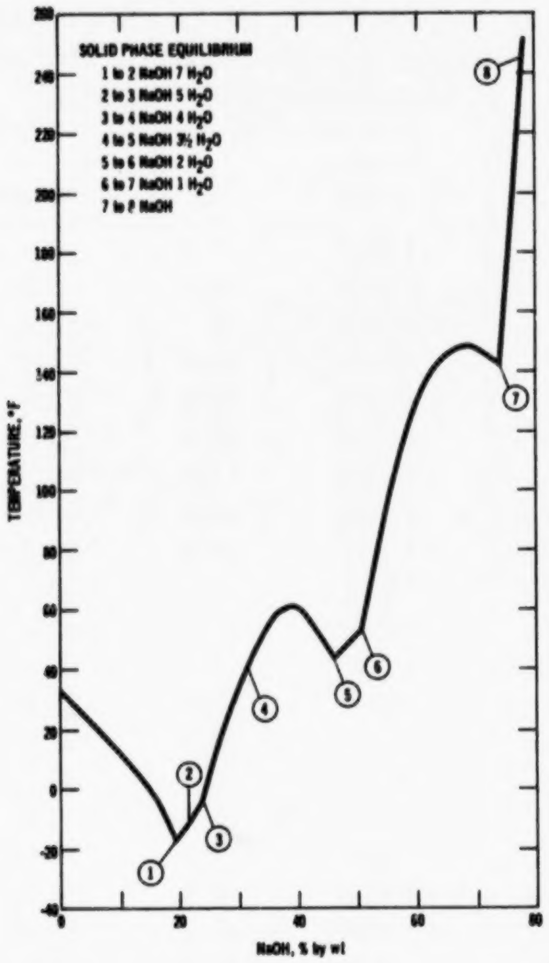


Figure C-6. Freezing points of caustic soda solutions.[37]

The vapor pressures of molten sodium solutions, taken from reference 15, are shown in Figure C-10.

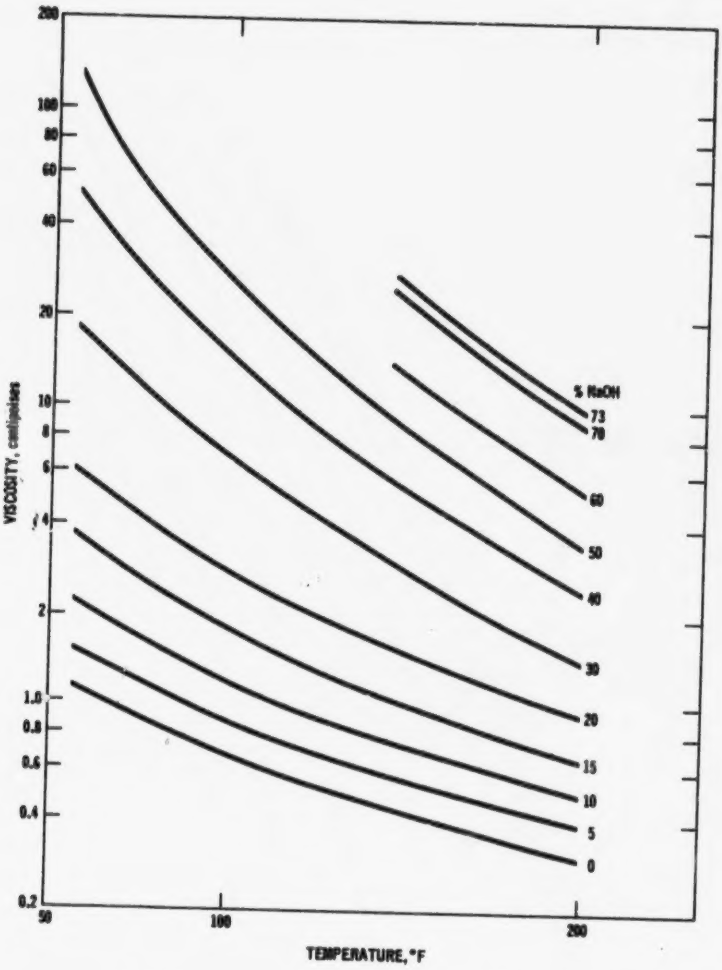


Figure C-7. Viscosity of caustic soda solutions.[37]

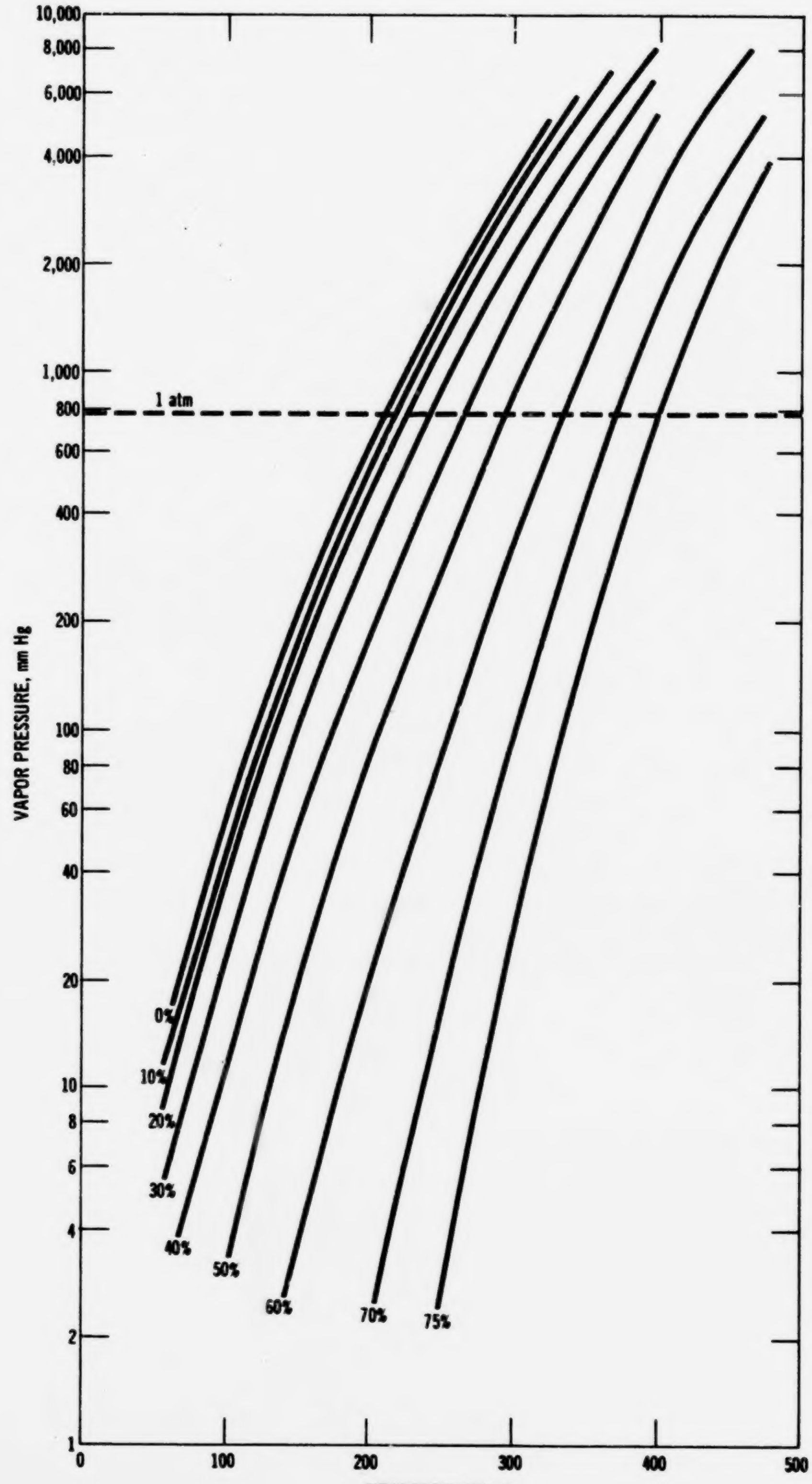
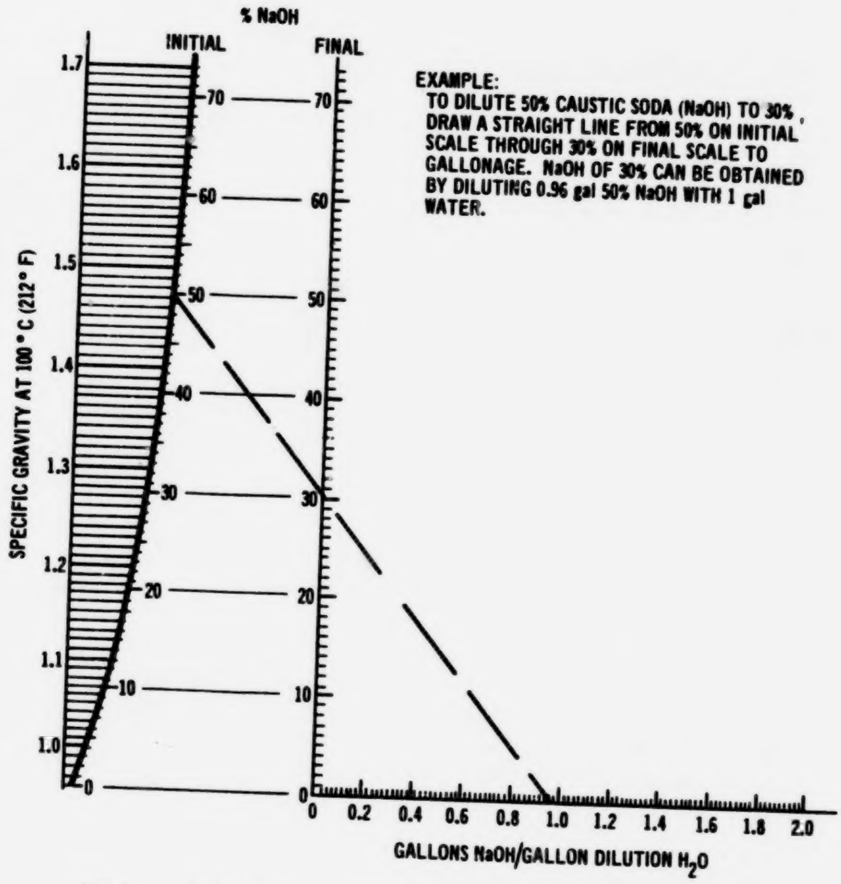


Figure C-8. Vapor pressure of caustic soda solutions.[37]



EXAMPLE:
TO DILUTE 50% CAUSTIC SODA (NaOH) TO 30%, DRAW A STRAIGHT LINE FROM 50% ON INITIAL SCALE THROUGH 30% ON FINAL SCALE TO GALLONAGE. NaOH OF 30% CAN BE OBTAINED BY DILUTING 0.96 gal 50% NaOH WITH 1 gal WATER.

Figure C-9. Caustic soda dilution nomograph.[37]

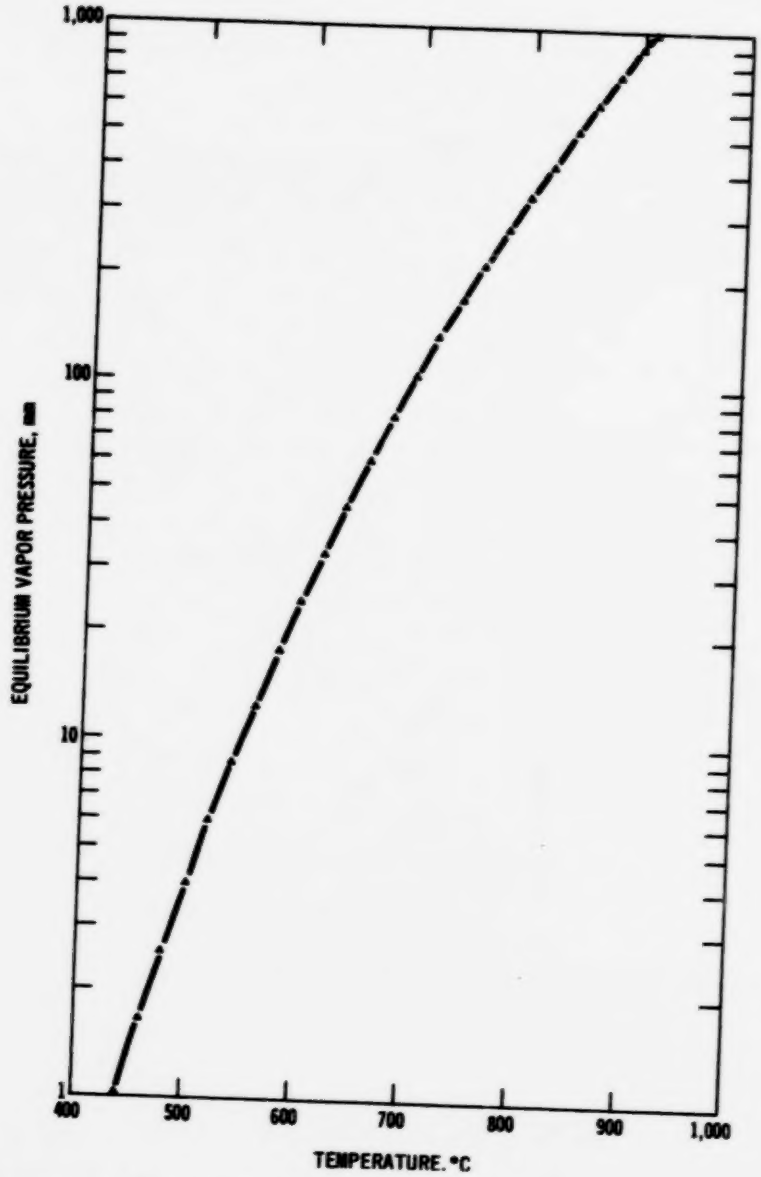


Figure C-10. Relationship of vapor pressure and temperature of liquid sodium.[15]

APPENDIX D. CHLORINE-CAUSTIC, FUSED-SALT, AND LIME-SODA ESTABLISHMENTS IN UNITED STATES, JANUARY 1970

Table D-1. CHLORINE PLANTS IN UNITED STATES[3]

Location	Producer	Year built[a]	Cells[b]
Alabama			
Huntsville	Stauffer Chemical Co. (leased from U.S. Government)	1943	Hooker S (D)
Le Moyne	Stauffer Chemical Co.	1965	De Nora 22 x 5 (M)
McIntosh	Olin Corp.	1952	Olin E8 (M)
Mobile	Diamond Shamrock Chemical Co.	1964	De Nora (M)
Muscle Shoals	Diamond Shamrock Chemical Co.	1952	De Nora 24 x 2M (M)
Arkansas			
Pine Bluff	(U.S. Government)	1943	Hooker S (D)
California			
Dominguez	Stauffer Chemical Co.	1963	BASF (M)
Pittsburg	The Dow Chemical Co.	1917	Dow (D), Dow (M)
Delaware			
Delaware City	Diamond Shamrock Chemical Co.	1965	De Nora 18 x 4 (M)
Georgia			
Augusta	Olin Corp.	1965	Olin E11F (M)
Brunswick	Allied Chemical Corp.	1957	Solvay V-100 (M)
Brunswick	Brunswick Chemical Co.	1967	Hooker S4 (D)
Illinois			
East St. Louis	Monsanto Co.	1922	De Nora 18 x 6 (M) (1962)
Kansas			
Wichita	Vulcan Materials Co.	1952	Hooker S, S3A, S3B (D)
Kentucky			
Calvert City	B.F. Goodrich Chemical Corp.	1966	De Nora 24H5 (M)
Calvert City	Pennwalt Corp.	1953	Olin E11F (1967) (M)
Louisiana			
Baton Rouge	Ethyl Corp.	1938	Downs (fused salt), Hooker S3D (D)
Baton Rouge	Allied Chemical Corp.	1937	Allen-Moore (modified) (D), (Hooker S4 (D) (1968)
Geismar	Wyandotte Chemicals Corp.	1959	Diamond D3 (D), Uhde 30 m^2 (M) (1964), Hooker S4 (D) (1969)
Gramercy	Kaiser Aluminum and Chemical Corp.	1958	Hooker S3B (D)
Lake Charles	PPG Industries Inc.	1947	Columbia N 1, Hooker S3A (D), De Nora 48H5 (M) (1969)
Plaquemine	The Dow Chemical Co.	1958	Dow (D), Solvay V-200 (M) (1963)
Taft	Hooker Chemical Corp.	1966	Hooker S4 (D)
Maine			
Orrington	IMC Chlor-Alkali Inc.	1967	De Nora 24H5 (M)
Rumford	Ethyl Corp. (Oxford Paper Div.)	1916	Sorensen (M)
Michigan			
Midland	The Dow Chemical Co.	1897	Dow (D)
Montague	Hooker Chemical Corp.	1954	Hooker S3A (D)
Wyandotte	Pennwalt Corp.	1898	Diamond D3 (D) (1960)
Wyandotte	Wyandotte Chemicals Corp.	1938	Hooker S3B (D), Wyandotte (M)
Mississippi			
Vicksburg	Southwest Potash Corp.	1962	None

Nevada			
Henderson	Stauffer Chemical Co. of Nevada Inc.	1942	Hooker S (D)
New Jersey			
Elizabeth	Maquite Corp.	1964	Maquite (M)
Linden	GAF Corp.	1956	Krebs (M) (1963); Mod. BASF-Krebs (1969)
Newark	Vulcan Materials Co.	1961	Hooker S (D), Hooker S4 (1968)
New York			
Niagara Falls	E.I. du Pont de Nemours and Co., Inc.	1898	Downs (fused salt)
Niagara Falls	Hooker Chemical Corp.	1898	Hooker S, S3A, Gibbs (modified) (D), Uhde 20 m^2 (M) (1961)
Niagara Falls	Int'l. Minerals and Chemical Corp.	1916	Hooker S (D)
Niagara Falls	Olin Corp.	1897	Olin E11F (M) (1960)
Niagara Falls	Stauffer Chemical Co.	1898	Hooker S, S3M (D)
Syracuse	Allied Chemical Corp.	1927	Allen-Moore (modified) (D), Solvay Process SD12 (M) (1946), Solvay S60 (M) (1953), Hooker S4 (D) (1968)
North Carolina			
Acme	Allied Chemical Corp.	1963	Solvay V-200 (M)
Canton	U.S. Plywood-Champion Papers, Inc.	1916	Hooker S (D)
Pisgah Forest	Olin, Ecusta Operations	1947	Sorensen (M)
Ohio			
Ashtabula	Detrex Chemical Industries, Inc.	1963	Olin E11F (M)
Ashtabula	Reactive Metals, Inc.	1949	Downs (fused salt)
Barberton	PPG Industries Inc.	1936	Columbia (D)
Painesville	Diamond Shamrock Chemical Co.	1928	Diamond D3 (D) (1959)
Oregon			
Portland	Pennwalt Corp.	1947	Gibbs (modified) (D) Diamond (D) 1957)
Tennessee			
Charleston	Olin Corp.	1962	Olin E11F, E812 (M)
Memphis	E.I. du Pont de Nemours and Co., Inc.	1958	Downs (fused salt)
Memphis	Velsicol Chemical Corp.	1943	Hooker S4 (D) (1969)
Texas			
Corpus Christi	PPG Industries Inc.	1938	Columbia N1, N3 (D)
Denver City	Vulcan Materials Co.	1947	Hooker S (D)
Freeport	The Dow Chemical Co.	1940	Dow (D)
Houston	U.S. Plywood-Champion Papers, Inc.	1936	Hooker S (D)
Deer Park (Houston)	Diamond Shamrock Chemical Co.	1938	Diamond (D), De Nora 18 SGL (M)
Houston	Ethyl Corp.	1952	Downs (fused salt)
Houston	Shell Chemical Co.	1966	Hooker S4 (D)
Point Comfort	Aluminum Co. of America	1966	De Nora 24 x 5 (M)
Port Neches	Jefferson Chemical Co., Inc.	1959	Hooker S3B (D)
Snyder	American Magnesium Co.	1969	
Virginia			
Hopewell	Hercules, Inc.	1939	Hooker S3 (D)
Saltville	Olin Corp.	1951	Olin E8 (M)
Washington			
Bellingham	Georgia-Pacific Corp.	1965	De Nora 18 x 4 (M)
Longview	Weyerhaeuser Co.	1957	De Nora 14 TGL & 24 H5 (M) (1967)
Tacoma	Hooker Chemical Corp.	1929	Hooker S3 (D)
Tacoma	Pennwalt Corp.	1929	Gibbs (modified) (D)

West Virginia			
Moundsville	Allied Chemical Corp.	1953	Solvay S60 (M)
New Martinsville	PPG Industries, Inc.	1943	Columbia N1, N3, N6 (D), Uhde 20 m^2 (D) (1958)
So. Charleston	FMC Corp.	1916	Hooker S3B (D) (1957), Hooker S4 (D) (1967)
Wisconsin			
Green Bay	Fort Howard Paper Co.	1968	Hooker S4 (D)
Port Edwards	Wyandotte Chemicals Corp.	1967	De Nora 24H5 (M)

[a] Refers to year chlorine production started at location.

[b] D = diaphragm cells; M = mercury cells.

Table D-2. SUMMARY OF CHLORINE-PRODUCING PLANTS[3]

Type of plant	Number of plants
Chlorine producers[a, b]	
Companies	35
Plants	69
Pulp mills producing chlorine[a] (included in A)	
Companies	6
Plants	7
Chlorine repackagers	
Companies	45
Plants	91
Cells	
Diaphragm-cell plants	27
Mercury-cell plants	25
Diaphragm- and Mercury-cell plants	10
Fused-salt cell plants	4
Non-electrolytic plants	1
Diaphragm- and fused-salt cell plants	1
Magnesium-cell plants	1

[a] Only those in operation.

[b] Daily capacity of 27,494 tons of gas as of November 1, 1969.

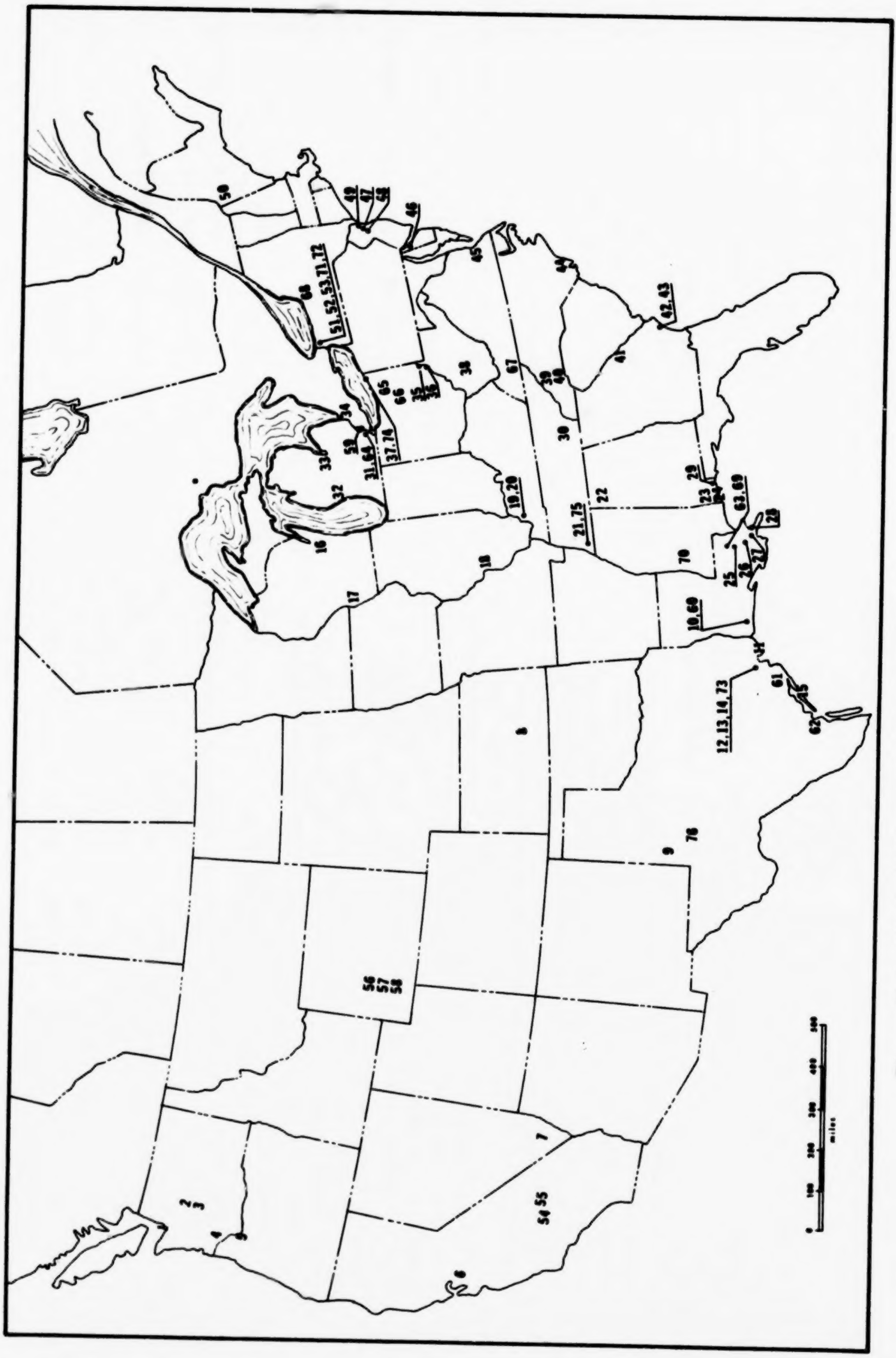

2
3
4
5
6
7
54 55
56
57
58
8
9
76
10,60
12,13,14,73
61
15
62
70
25
26
27
28
63,69
23
24
29
22
21,75
18
19,20
17
16
32
33
31,64
37,74
34
65
66
35
36
38
30
39
40
67
41
42,43
44
45
46
47
48
49
50
51,52,53,71,72
68
0
100
200
300
400
500
miles

Figure D-1. United States chlorine and alkali producers, January 1, 1970.

CHLORINE AND SODA ASH

1. GEORGIA-PACIFIC–Bellingham, Wash.
2. HOOKER–Tacoma, Wash.
3. PENNWALT–Tacoma, Wash.
4. WEYERHAEUSER–Longview, Wash.
5. PENNWALT–Portland, Oregon
6. DOW–Pittsburg, Calif.
7. STAUFFER–Henderson, Nevada
8. VULCAN–Wichita, Kansas
9. VULCAN–Denver City, Texas
10. PPG–Lake Charles, La.
11. JEFFERSON–Port Neches, Texas
12. DIAMOND–Houston, Texas
13. U.S. PLYWOOD-CHAMPION–Houston, Texas
14. SHELL–Houston, Texas
15. ALCOA–Pt. Comfort, Texas
16. FT. HOWARD–Green Bay, Wis.
17. WYANDOTTE–Port Edwards, Wis.
18. MONSANTO–East St. Louis, Ill.
19. GOODRICH–Calvert City, Ky.
20. PENNWALT–Calvert City, Ky.
21. VELSICOL–Memphis, Tenn.
22. DIAMOND–Muscle Shoals, Ala.
23. OLIN–McIntosh, Ala.
24. DIAMOND–Mobile, Ala.
25. DOW–Plaquemine, La.
26. WYANDOTTE–Geismar, La.
27. KAISER-ALUMINUM–Gramercy, La.
28. HOOKER–Taft, La.
29. STAUFFER–Lemoyne, Ala.
30. OLIN–Charleston, Tenn.
31. PENNWALT–Wyandotte, Mich.
32. HOOKER–Montague, Mich.
33. DOW–Midland, Mich.
34. DOW–Sarnia, Ont., Canada
35. ALLIED–Moundsville, Ohio
36. PPG–New Martinsville, W. Va.
37. DETREX–Ashtabula, Ohio
38. FMC CORP.–South Charleston, W. Va.
39. U. S. PLYWOOD-CHAMPION–Canton, N. C.
40. ECUSTA OPERATIONS, OLIN–Pisgah Forest, N. C.
41. OLIN–Augusta, Ga.
42. ALLIED–Brunswick, Ga.
43. BRUNSWICK CHEM.–Brunswick, Ga.
44. ALLIED–Acme, N. C.
45. HERCULES–Hopewell, Va.
46. DIAMOND–Delaware City, Del.
47. MAQUITE–Elizabeth, N. J.
48. GAF–Linden, N. J.
49. VULCAN–Newark, N. J.
50. ETHYL–Rumford, Me.
51. HOOKER–Niagara Falls, N. Y.
52. OLIN–Niagara Falls, N. Y.
53. STAUFFER–Niagara Falls, N. Y.

SODA ASH

54. AMERICAN POTASH AND CHEM.–Trona, Calif.
55. STAUFFER–West End, Calif.
56. ALLIED–Green River, Wyo.
57. STAUFFER–Green River, Wyo.
58. FMC CORP.–Green River, Wyo.
59. ALLIED–Amherstburg, Ont., Canada
60. OLIN–Lake Charles, La.

CHLORINE, CAUSTIC SODA, SODA ASH

61. DOW–Freeport, Texas
62. PPG–Corpus Christi, Texas
63. ALLIED–Baton Rouge, La.
64. WYANDOTTE–Wyandotte, Mich.
65. DIAMOND–Painesville, Ohio
66. PPG–Barberton, Ohio
67. OLIN–Saltville, Va.
68. ALLIED–Syracuse, N. Y.
69. ETHYL–Baton Rouge, La.

CHLORINE

70. SOUTHWEST POTASH–Vicksburg, Miss.

CHLORINE AND CAUSTIC POTASH

71. INT. MIN. AND CHEM.–Niagara Falls, N. Y.

CHLORINE AND SODIUM

72. DUPONT–Niagara Falls, N. Y.
73. ETHYL–Houston, Texas
74. REACTIVE METALS–Ashtabula, Ohio
75. DUPONT–Memphis, Tenn.

CHLORINE AND MAGNESIUM

76. AMERICAN MAGNESIUM–Snyder, Texas

APPENDIX E. FIELD TEST OF ABSORPTION EFFICIENCY OF BLOW-GAS ABSORBER

Plant 30, a diaphragm-cell plant (see Tables 6 and D-1), was operated under several sets of conditions to permit calculation of absorption efficiencies of the water absorber at several different simulated plant operating rates. This was accomplished by keeping the water circulation constant at the maximum practical rate and varying the amount of blow gas fed into the scrubber, thus changing the liquid/gas ratio in order to determine its effects on absorption efficiency. Table E-1 was developed from the test data obtained.

The blow-gas absorber in this plant is part of an integrated system having the dual purpose of cooling cell gas and recovering chlorine from blow gas. The main factors in the operation are the quantity of water circulated and the quantity of steam required to complete stripping of the chlorine to the desired level in the discarded water stream (Figure 10). Since at a constant plant capacity (e.g., 100 tons per day) the blow-gas rate may be expected to be constant, and, therefore, to impose a constant heat load on the system, the incremental quantities of steam required to heat water to stripping temperatures at various water rates can be easily calculated as follows:

First, reduce the test data to a constant production rate of 100 tons per day.

	Test			
	1	2	3	4
Chlorine absorbed, lb/hr	129.4	164.5	176.1	180.5
Residual chlorine in vent, lb/hr	51.7	16.1	4.43	1.034
Absorption efficiency, %	72.5	91.0	97.4	99.4
Absorber water rate, 1000 lb/hr	32.1	33.1	37.8	47.3

Second, from the data above, calculate: (1) the additional water required for Test 2 as compared with Test 1: 33,100 - 32,100 = 1000 lb/hr; (2) similarly, for Test 3 with respect to Test 2: 37,800 - 33,100 = 4700 lb/hr; and (3) for Test 4 with respect to Test 3: 47,300 - 37,800 = 9500 lb/hr.

Similarly, calculate the incremental amounts of chlorine absorbed: (1) Test 2 - Test 1 = 164.5 - 129.4 = 35.1 lb/hr; (2) Test 3 - Test 2 = 176.1 - 164.5 = 11.6 lb/hr; and (3) Test 4 - Test 3 = 180.5 - 176.1 = 4.4 lb/hr.

The incremental amount of water required to recover an incremental amount of chlorine can now be calculated: (1) Test 2 - Test 1 = 1000/35.1 =

Table E-1. TESTS OF BLOW-GAS ABSORBER EFFICIENCY

	1	2	3	4
Equivalent plant capacity, tons Cl_2/day (based on total pounds of chlorine to absorber)	180.0	170.0	149.0	119.0
Chlorine in blow gas, lb/hr	326.0	307.0	269.0	216.0
Chlorine absorbed, lb/hr	233.0	279.6	262.4	214.77
Residual chlorine in vent, lb/hr	93.0	27.4	6.6	1.23
Absorption efficiency, %	72.5	91.0	97.4	99.4
Water rate to absorber, 1000 lb/hr	57.8	56.3	56.3	56.3
Water/chlorine ratio, lb/lb chlorine absorbed	248.1	201.4	214.6	262.1

28.5 lb of water/lb of chlorine; (2) Test 3 - Test 2 = 4700/11.6 = 405 lb of water/lb of chlorine; and (3) Test 4 - Test 3 = 9500/4.4 = 2159 lb of water/lb of chlorine.

The amount of steam required to heat the incremental quantities of water from feed temperature (24.5° C) to stripping temperature (97° C) can be easily calculated as follows:

$$\frac{(97 - 24.5)(9/5)}{1000} = 0.1305 \text{ lb steam/lb water circulated.}$$

Although additional steam is also required to vaporize the incremental pound of chlorine in removing it from the water solution, the latent heat of chlorine is so small in relation to that of steam (about 1:10) that this can be neglected in the calculation. Results can be summarized as shown in Table E-2.

These results are also plotted in Figure E-1.

Determination of the point at which it is no longer economical to recover further chlorine can easily be calculated from these values by assigning values

Table E-2. WATER AND STEAM NEEDED TO INCREASE ABSORBER EFFICIENCY

To increase efficiency		Lb additional water needed/lb chlorine recovered	Lb additional steam needed/lb chlorine recovered
From, %	To, %		
72.5	91.0	28.5	3.72
91.0	97.4	405.0	52.9
97.4	99.4	2159.0	282.0

for the cost of water, steam, and chlorine. When the cost of incremental water and steam is equivalent to the value of the chlorine recovered, the optimum operating point has been reached. Obviously, a water absorber can be operated above the economical optimum to reduce a pollution problem. Consideration of values similar to those noted in this example will permit the selection of desirable operating conditions.

It is also possible to scrub vent gas from the main water absorber in a second unit from which the water is discarded. This requires no additional steam and chlorine absorbed in the waste water is sufficiently dilute that usually no problem with liquid waste disposal is encountered. This method is generally preferable to passing vent gases to a caustic scrubber where the carbon dioxide in the vent gas will consume a large amount of additional caustic.

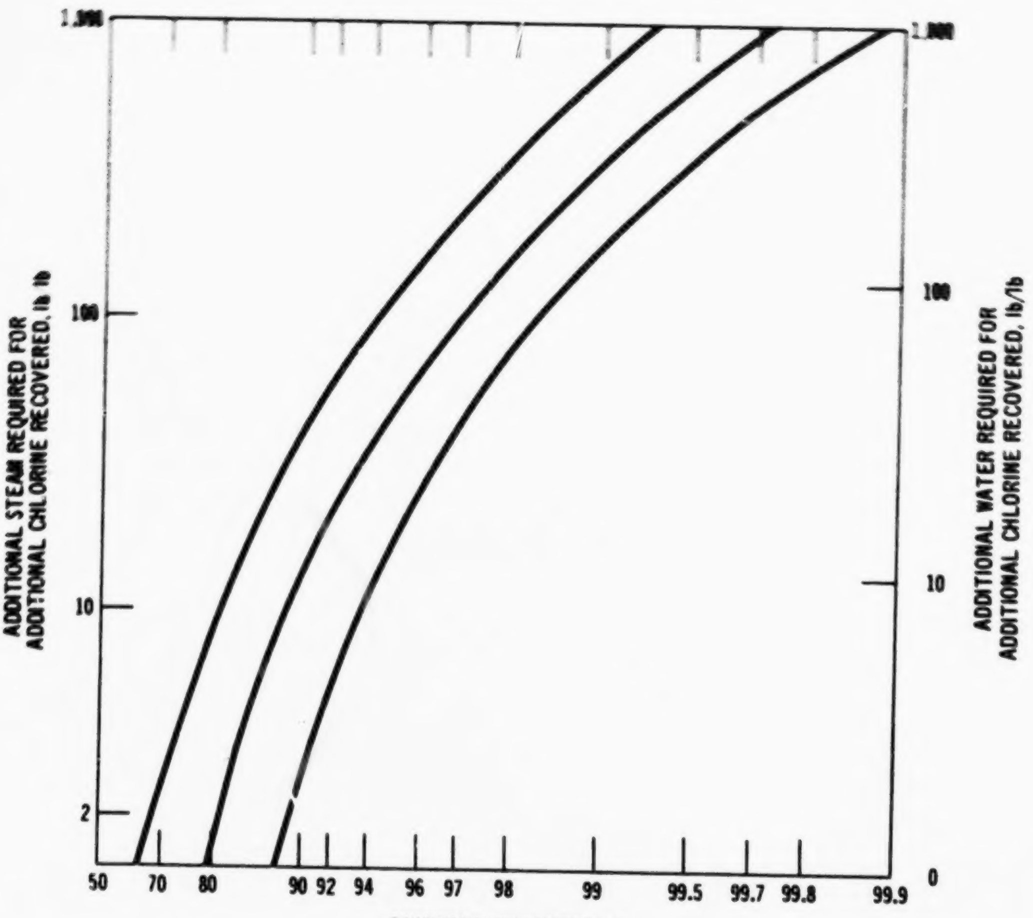


Figure E-1. Water and steam required to increase blow-gas absorber efficiency.

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